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Supplemental Groundwater Tracing Summary Report Arkwood, Inc. Superfund Site, Omaha, Arkansas

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1 INTRODUCTION

The Ozark Underground Laboratory, Inc. (OUL) on behalf of McKesson Corporation conducted the supplemental groundwater tracing study described in this report as part of ongoing groundwater remediation activities at the Arkwood, Inc. Superfund Site (Site) in Omaha, Arkansas. The study was conducted in compliance with the Final Supplemental Groundwater Tracing Study Work Plan (Work Plan) dated October 7, 2014 (Aley 2014) that was approved by the U.S. Environmental Protection Agency (USEPA) on October 21, 2014. Appendix D provides a copy of the Work Plan (without attachments).

1.1 Purpose and Scope of Study

In March 2014 McKesson Corporation hosted a tour of the Site and facilitated an on-Site discussion with personnel from the USEPA and the Arkansas Department of Environmental Quality (ADEQ). One topic raised during the tour was the potential benefit of conducting a semi-quantitative dye trace from the vicinity of a former on-Site sinkhole to New Cricket Spring. Such a trace would provide data about water movement from that portion of the Site most heavily impacted by historical operations to New Cricket Spring, the location where contaminated groundwater emanating from the Site discharges to the surface. The Work Plan (see Appendix D) presented the tracer study's proposed scope and procedures. The following tasks were performed as part of the study:

- Introduce two tracer dyes into two separate shallow wells in the epikarstic zone near the former on-Site sinkhole (one dye into each well);
- Periodically collect composite water samples and flow rate measurements from New Cricket Spring to permit calculation of a semi-quantitative mass balance; and
- Collect activated carbon samples and grab water samples in selected locations in both the Cricket Creek and Walnut Creek watersheds to determine if any detectable concentration of either of the dyes discharges to any locations in addition to New Cricket Spring.

1.2 Site Background

Historically a wood preservative treating facility was operated at the Arkwood Site. Pentachlorophenol (PCP) and dioxin-containing wastes were discharged to a small sinkhole at the Site during at least a portion of the Site operations. As much debris as possible was removed from the sinkhole during remediation activities in the mid-1990s. The sinkhole was then filled with concrete. In 1997, a water treatment system was constructed near the mouth of New Cricket Spring, which is located downgradient and off-Site. The system continues to collect and treat groundwater discharging from New Cricket Spring. In 2005, eleven shallow wells were installed into the top of the epikarstic zone near the former sinkhole and ozonated water was introduced into some of the wells in an effort to expedite treatment of residual PCP

concentrations in the subsurface. Injections of ozonated water continued until 2010; non-ozonated water was injected from 2010 through 2012.

1.3 Hydrogeologic Setting

The Arkwood Site is located on relatively flat-lying Boone Formation of Mississippian age. The Boone Formation is comprised primarily of limestone with varying amounts of chert. The abundance of chert varies both laterally and vertically within the formation. The upper portion of the limestone bedrock surface is called the epikarst or epikarstic zone. This zone in the Boone Formation is often about 30 feet thick with the abundance of solutional voids decreasing with depth.

The epikarstic zone has been modified by solution and by partial in-filling with sediments derived from dissolution of the bedrock and from overlying soil and residuum. The former sinkhole was a feature within the epikarstic zone and New Cricket Spring is the discharge point for groundwater from the vicinity of the former sinkhole.

The flow rates for New Cricket Spring and the volume of water detained in the epikarstic zone vary both rapidly and dramatically as a result of precipitation events. For example, the historic flow rates of New Cricket Spring have varied by about three orders of magnitude. In addition, during much of the year, most of the epikarstic zone at the Arkwood Site is unsaturated. This is demonstrated by the frequent absence of water in the eleven shallow wells constructed into the epikarstic zone in the vicinity of the former sinkhole.

The majority of groundwater flow occurs in only a portion of the total pore space; this is known as the mobile porosity. In the epikarstic setting found at the Arkwood Site, residual contaminants are largely retained in the non-mobile portion of the aquifer porosity and slowly diffuse into the waters discharging from New Cricket Spring. This is consistent with the continued discharge of residual PCP in water emanating from New Cricket Spring. Sutherson et al. (2014) note that presumptive values for mobile porosity as recommended in regulatory guidelines have been 20%. Although seldom measured, higher values for mobile porosity are likely to occur in at least some karst aquifers or aquifer segments. The semi-quantitative dye tracing investigation discussed in this report provides a valuable on-Site measurement of the percent of mobile porosity existing in the most impacted portion of the shallow epikarstic zone aquifer at the Arkwood Site.

1.4 Previous Groundwater Tracing Study

In 1991 the OUL conducted a comprehensive groundwater tracing study at the Arkwood Site with 79 off-Site sampling stations (Aley 1992). Dyes for that study were introduced at two locations that effectively bracketed the Site. Table 1 summarizes details of the 1991 traces.

Table 1. Previous Dye Traces. From Aley (1992).

Trace No.	Dye Introduction Location	Dye Mixture Type & Quantity	Detection Locations
91-01	Woodchip Pile Trace (SE corner of the site)	10 lbs Fluorescein 28.5 lbs Rhodamine WT	12 stations in Walnut Creek Valley
91-02	New Cricket Spring Trace (spring branch)	10 lbs Fluorescein 28.5 lbs Rhodamine WT	14 stations within or near channels of New Cricket Spring Branch and Cricket Creek

The dye equivalent in the fluorescein mixture used in the 1991 tracing was 75%. It was 20% in the rhodamine WT mixture. The 1991 tracing demonstrated that the Site was underlain by a groundwater divide. Groundwater from the southeastern portion of the Site discharges to the Walnut Creek topographic basin and groundwater from the northwestern portion of the Site discharges to the Cricket Creek topographic basin.

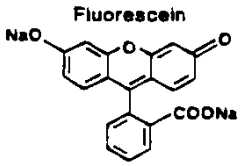
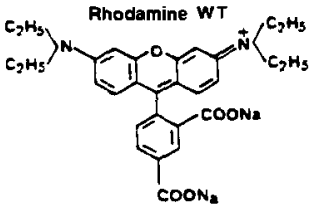
2 METHODOLOGY

Groundwater tracing using fluorescent dyes is an ideal method for identifying groundwater flow paths and characterizing their functioning in karst areas such as the Arkwood Site. This section provides an overview of the dye introduction, sampling, and laboratory procedures used during this supplemental groundwater tracing study.

2.1 Dye Introductions

Fluorescein and rhodamine WT dyes were used for two separate dye introductions during the supplemental groundwater tracing study. Both of these dyes are environmentally safe and pose no risk to humans, livestock, or to aquatic life in the concentrations used in professionally-directed groundwater tracing work (Smart 1984, Field et al. 1995). Table 2 illustrates the chemical structures of these dyes and summarizes some of their more important properties.

Table 2. Properties of Tracer Dyes Used In This Study.

Fluorescein Dye • Also known as Acid Yellow 73 • Color Index Constitution Number 45350 • Brilliant fluorescent yellow-green dye • Most commonly used fluorescent tracer dye • Most highly detectable dye • Powdered dye, 75% dye equivalent, 25% diluent	
Rhodamine WT Dye • Also known as Acid Red 388 • Color Index Constitution Number not assigned • Reddish orange-colored dye • Less resistant to adsorption onto aquifer materials than fluorescein and eosine	

These dyes are among the most detectable of the commonly used fluorescent tracer dyes. They can be adsorbed onto activated carbon samplers for cumulative sampling and can also be detected in water samples.

The results of the dye introductions performed as part of this supplemental study were used for characterizing flow paths, identifying discharge points, and creating a semi-quantitative mass balance. Both dye introductions were made specifically for this study. The traces are numbered sequentially with the first two digits indicating the year and the last pair of digits indicating the serial number of the trace. The dye introduction locations and the amount and type of dye used are

summarized in Table 3. The fluorescein mixture contained 75% dye equivalent and the rhodamine WT mixture contained 20% dye equivalent.

Table 3. 2014 Dye Introductions.

Trace No.	Dye Introduction Location	Dye Mixture Type & Quantity	Dye Introduction Date & Time
14-01	Former Sinkhole Area Well A	1 lb Fluorescein	11-17-2014 1315
14-02	Former Sinkhole Area Well B	4 lb Rhodamine WT	11-17-2014 1308

2.2 Sampling for Tracer Dyes

This section describes the types of tracer dye sampling performed during this study. All samples were collected and analyzed by OUL staff in Protem, Missouri. The Work Plan for the study (see Appendix D) provides a site map and a sketch map showing the locations of the wells utilized in the sinkhole area.

2.2.1 Types of Samples

Three kinds of fluorescent tracer dye samples were collected during the project: activated carbon samplers, grab water samples, and composite water samples.

The activated carbon samplers consist of fiberglass screen wire packets filled with 4.25 grams of laboratory-grade activated coconut shell carbon. These samplers adsorb, retain, and concentrate the tracer dyes. When eluted in the laboratory, samples routinely yield dye concentrations one to two or more orders of magnitude greater than the mean dye concentrations in the water. Activated carbon samplers are continuous and accumulating samplers.

Grab samples of water provide dye concentrations at particular points in time. Water samples are collected in 50-milliliter plastic sampling vials at all sampling stations where practical and are archived upon receipt at the lab. Water samples are typically analyzed for the following reasons:

- to corroborate the dyes detected in the associated activated carbon samplers,
- to provide supplemental data when an activated carbon sampler is lost and/or is not retrievable, and
- to corroborate data with fluorescence or rhodamine WT peaks in the associated carbon sampler

Composite water samples were collected at New Cricket Spring with an ISCO automatic pump sampler. For the first two weeks following the dye introduction, eight hourly subsamples were collected into each composite water sample resulting in three composite water samples collected each day for continuous monitoring of the spring. For weeks three through seven

following the dye introduction, 12 hourly subsamples were collected into each composite water sample resulting in two composite water samples per day. Composite water samples were collected to permit a mass balance calculation for each tracer dye. This information permits a measurement of the percent of mobile porosity in the portion of the epikarstic aquifer lying between the former sinkhole and New Cricket Spring. The information also provides an improved understanding of groundwater travel rates and the historic movement of contaminants through this portion of the aquifer.

Because of cold weather conditions and the critical importance of the data, OUL installed and operated two ISCO samplers at New Cricket Spring as a redundancy in the event one failed; both functioned perfectly so only samples from the primary sampler were analyzed. Both ISCO samplers were enclosed in a heated shelter near the spring.

All sample collection procedures followed the protocols found in OUL's Procedures and Criteria document (Aley and Kirkland 2011), which is attached as Appendix A.

2.2.2 Sampling Locations

Twenty sampling locations were established for the supplemental dye tracing study. Sampling locations consisted of springs, wells, and stream locations. Background samples were also collected from the water sources used in the study. Table 4 identifies sampling stations, and Table 5 compares station numbers and names. Their locations are shown in Figure 1 on page 10.

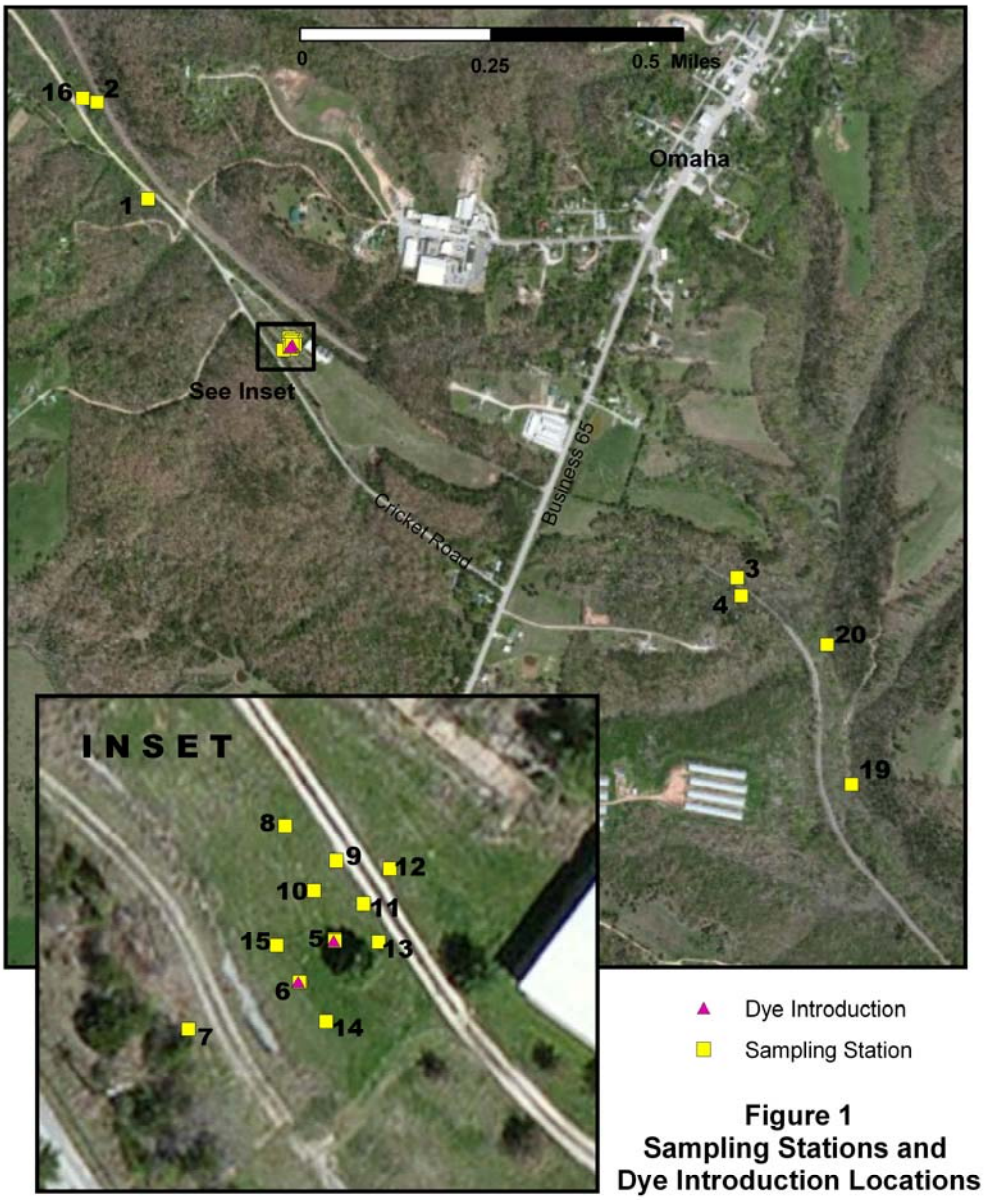
Table 4. Sampling Stations for the Arkwood Tracer Study.

Station No.	Station Name	Location Type	Topographic Basin
1	New Cricket Spring	Spring	Cricket Creek
2	Cricket Spring	Spring	Cricket Creek
3	Railroad Tunnel SE; total drainage, east side	Spring Flow	Walnut Creek
4	Railroad Tunnel SE; total drainage, west side	Spring Flow	Walnut Creek
5	Well A	Monitoring well	Cricket Creek
6	Well B	Monitoring well	Cricket Creek
7	Well C	Monitoring well	Cricket Creek
8	Well D	Monitoring well	Cricket Creek
9	Well E	Monitoring well	Cricket Creek
10	Well F	Monitoring well	Cricket Creek
11	Well G	Monitoring well	Cricket Creek
12	Well H	Monitoring well	Cricket Creek
13	Well I	Monitoring well	Cricket Creek
14	Well J	Monitoring well	Cricket Creek
15	Well K	Monitoring well	Cricket Creek
16	Cricket Pond Discharge	Surface water	Cricket Creek
17	Deep Well Water	Background	Cricket Creek
18	City Water – hose	Background	--
19	Walnut Creek Valley Spring	Spring	Walnut Creek
20	Walnut Creek – North	Stream	Walnut Creek

Table 5. Comparison of station numbers and names between the 1991 and 2014 tracer studies.

2014 Study		1991 Study	
1	New Cricket Spring	17	New Cricket Spring
2	Cricket Spring	21	Old Cricket Spring
3	RR Tunnel SE; total drainage, east side	3E	Railroad tunnel; total drainage east side
4	RR Tunnel SE; total drainage, west side	3W	Railroad tunnel; total drainage west side
5	Well A	--	Not sampled
6	Well B	--	Not sampled
7	Well C	--	Not sampled
8	Well D	--	Not sampled
9	Well E	--	Not sampled
10	Well F	--	Not sampled
11	Well G	--	Not sampled
12	Well H	--	Not sampled
13	Well I	--	Not sampled
14	Well J	--	Not sampled
15	Well K	--	Not sampled
16	Cricket Pond Discharge	--	Not sampled
17	Deep Well Water	15	Arkwood deep well
18	City Water	--	Not sampled
19	Walnut Creek Valley Spring	7	Walnut Creek Valley Spring
20	Walnut Creek - North	5	North Tributary to Walnut Creek

Figure 1. Map Showing Dye Introduction Points and Sampling Stations.



All monitoring wells were located in the former sinkhole area on-Site. The depth to water and total depth of the wells were measured during the field reconnaissance (Table 6). Samples were collected at all wells prior to the dye introduction, one week following the dye introduction, and at the end of the study. Additional samples were collected at intermediate sampling events in wells that contained water. Water was primarily observed in wells that had leaking valves associated with the former injection system. Most of the wells were dry during most of the study.

Table 6. Former Sinkhole Area Well Measurements – Total Depth and Depth to Water. Total Depth measurements made on November 7, 2014. Units in feet below top of casing (ft bTOC).

Sample Station	Total Depth	11/7/14	11/17/14	11/24/14	12/22/14
Well A	31.50	30.31	30.33	31.50	23.76
Well B	23.85	Dry	Dry	Dry	Dry
Well C	30.0	Dry	Dry	Dry	Dry
Well D	4.35	Dry	Dry	Dry	Dry
Well E	12.85	12.85	8.83	8.66	8.91
Well F	13.50	9.92	6.81	6.70	6.93
Well G	12.20	Dry	Dry	Dry	Dry
Well H	5.11	Dry	Dry	Dry	Dry
Well I	9.25	Dry	Dry	Dry	Dry
Well J	14.35	Dry	Dry	7.78	6.40
Well K	16.72	Dry	Dry	Dry	15.71

2.2.3 Sampling Events

Background sampling was performed to detect and quantify the presence of tracer dyes or fluorescent compounds with characteristics similar to tracer dyes. Background sampling was performed with charcoal samplers and grab water samples. Background sampling occurred from November 7 to November 17, 2014. This was prior to dye introductions.

Sampling for tracer dyes followed dye introductions. Sampling was weekly at most stations. Weekly sampling events following dye introductions occurred from November 24, 2014 to January 5, 2015. One additional sampling event occurred on January 23, 2015 when a limited number of charcoal samplers were collected.

2.2.4 Sample Collection Procedures

Activated Carbon Samplers and Grab Water Samples. Activated carbon samplers located at springs and along surface streams were placed in flowing water or in locations anticipated to have flowing water during storm events. Samplers were firmly anchored with plastic tie wire and weighted in place. In some locations, cords were run from the packets to trees along the banks or other stationery objects so that samplers could be recovered in case of relatively high flow events. Samplers were concealed to minimize disturbance or vandalism. A minimum of two samplers were placed at each surface water sampling station. Placement of

multiple samplers allows for the analysis of duplicate samples, if needed, and provides a spare in case a sampler is lost or damaged.

New samplers were placed when used carbon samplers were collected. Collected samplers were placed in sterile plastic bags. The bags were labeled on the outside with the station name and the date and time of collection. Grab samples of water were collected at the same time the activated carbon samplers were collected. Custody sheets were maintained for all samples.

Composite Water Samples Composite water samples were collected with ISCO automatic pump samplers. The automatic pump samplers were installed within the locked gate near the New Cricket Spring discharge location. The ISCO samplers were programmed to collect one subsample per hour. For the first two weeks following the dye introduction, eight hourly samples were composited into one sample container, so that three composite samples were collected during each 24-hour period. For weeks three through seven following the dye introduction, 12 hourly subsamples were composited into one sampling container so that two samples were collected per 24-hour period. The automatic sampler units were serviced once per week.

Samples collected in the field were maintained under refrigeration until delivery to the laboratory. Upon arrival at OUL, samplers were refrigerated until analysis. All sampler placement, collection, and analysis work was conducted by OUL personnel and conformed to the protocol in Appendix A (Aley and Kirkland 2011).

2.3 Laboratory Analysis

Laboratory analysis was performed at the OUL in Protem, Missouri. Activated carbon samples were rinsed under a relatively strong jet of water and eluted in a standard eluting solution. Water samples were pH adjusted to raise the pH of the water to 9.5 or higher. Elutant and pH-adjusted water samples were analyzed on a Shimadzu RF-5301 spectrofluorophotometer under a synchronous scanning protocol. All dye concentrations were based on the as-sold weight of dye mixtures.

Low concentrations of naturally-occurring fluorescent compounds with fluorescence characteristics similar to tracer dyes can be found in some areas. Background sampling prior to the introduction of tracer dyes is routinely performed to characterize background fluorescence and to identify the existence of any residual tracer dyes from prior studies that may be present.

The OUL has established normal emission fluorescence wavelength ranges for the dyes used in this supplemental study (fluorescein and rhodamine WT). The normal acceptable range equals mean values plus and minus two standard deviations (see Table 7). These values are derived from actual groundwater tracing studies conducted by the OUL.

The detection limits are based upon concentrations of dye necessary to produce emission fluorescence peaks where the signal to noise ratio is 3. The detection limits are realistic for most field studies since they are based upon results from actual field samples rather than being based upon values from spiked samples in a matrix of reagent water or the elutants from unused activated carbon samplers. In some cases detection limits may be lower than reported if the water being sampled has very little fluorescent material in it. In some cases detection limits may be higher than reported; this most commonly occurs if the sample is turbid due to suspended material or a coloring agent such as tannic compounds.

Normal emission wavelength ranges and detection limits for the dyes reported in this study when analyzed on the OUL's RF-5301 spectrofluorophotometer are shown in Table 7. Detailed procedures and criteria used during this supplemental tracer study are found in the OUL's Procedures and Criteria Document, Appendix A (Aley and Kirkland 2011).

Table 7. Spectrofluorophotometer Normal Emission Wavelength Ranges and Detection Limits for Fluorescein and Rhodamine WT Dyes in Water and Carbon Sampler Elutants.

Dye and Matrix	Normal Acceptable Emission Wavelength Range nanometers (nm)	Detection Limit (ppb)
Fluorescein in Elutant	514.5 to 519.6	0.025
Fluorescein in Water	506.8 to 510.6	0.002
Rhodamine WT in Elutant	565.2 to 571.8	0.170
Rhodamine WT in Water	572.4 to 577.7	0.015

Note: Detection limits are based upon the as-sold weight of the dye mixtures used by the OUL.

2.4 Precipitation and Flow Rate Measurements

Precipitation data for the study period were obtained from the Weather Underground (www.wunderground.com) station at Harrison, Arkansas. This station is approximately 20 miles south of Omaha.

Flow rates were measured with a pressure transducer installed at a weir near the spring mouth. Measurements were recorded hourly in gallons per minute (gpm). Measured flow rates were used along with ISCO automatic pump water sample results to make mass balance calculations.

3 STUDY RESULTS

Results are summarized under the following headings:

1) Precipitation and Flow Rate Measurements;
2) Supplemental Groundwater Tracing Results; and
3) Calculations.

3.1 Precipitation and Flow Rate Measurements

Precipitation data and daily average flow rate measurements for the study period are shown in Table 8. Relatively low flow conditions existed during the study, which are consistent with the late fall and winter season. The increased flow rate at the beginning of the study reflected water introduced artificially by OUL into the dye introduction wells.

As expected, precipitation events resulted in corresponding increases in flow from New Cricket Spring. Three primary precipitation events resulted in increased flows at the spring. The largest precipitation event, resulting in the largest flow from the spring, occurred at the end of the study.

3.2 Supplemental Groundwater Tracing

Two dye introductions were made during this study to provide more detailed information about groundwater flow from the former sinkhole area on-Site to New Cricket Spring. The results of these traces are described in this section.

The comprehensive analytical results are included in tabular form in Appendix B. Smaller tables within the text include dye analysis results for sampling stations where dyes from groundwater traces conducted as part of this investigation were detected. Dye concentrations are reported in parts per billion (ppb). Within the tables, the following abbreviations are routinely encountered: “ND” means that no dye was detected (see Table 7 for detection limits) and “nm” is an abbreviation for nanometers.

Charcoal samplers are continuous and accumulating samplers left in place for a period of time (most often one week). The “total” concentration is the amount of dye accumulated during the entire sampling period. When duplicate samplers were analyzed, the mean of the primary and the duplicate samplers is reported. Since sampling periods often vary due to field conditions, weather, and scheduling, a mean concentration-per-day has also been calculated. This average daily concentration is the total concentration divided by the number of days the sampler was left in place. This calculated mean concentration-per-day value provides more easily comparable concentration data from the charcoal samplers. A grab sample of water was

collected when the activated carbon samplers were collected. The corresponding water sample concentration is provided for the collection date of each charcoal sampler.

Table 8. Precipitation and Flow Rate Measurements.
Precipitation data in inches from Harrison, Arkansas; Flow rate data in gallons per minute (gpm).

Date	November 2014		December 2014		January 2015	
	Precipitation (in)	**Mean Flow Rate** (gpm)	**Precipitation** (in)	**Mean Flow Rate** (gpm)	**Precipitation** (in)	**Mean Flow Rate** (gpm)
1	0	NM	0	1.88	0	4.65
2	0	NM	0.04	2.08	0.05	5.94
3	0	NM	0.02	1.09	0.69	78.48
4	0	NM	0.01	1.93	0.52	46.46
5	0.01	NM	0.09	19.76	0	31.53
6	0	NM	1.13	28.25	--	NM
7	0	NM	0	17.56	--	NM
8	0.11	NM	0	11.06	--	NM
9	0	NM	0	7.51	--	NM
10	0	NM	0	5.99	--	NM
11	0	NM	0.01	4.98	--	NM
12	0	NM	0.07	4.75	--	NM
13	0	NM	0.01	4.61	--	NM
14	0	NM	0	4.58	--	NM
15	0	NM	0.48	17.77	--	NM
16	0	NM	0.14	13.33	--	NM
17	0.01	5.69	0	11.17	--	NM
18	0.04	8.80	0.58	26.70	--	NM
19	0	3.65	0	20.23	--	NM
20	0	2.34	0.02	14.88	--	NM
21	0	2.42	0.01	11.58	--	NM
22	0	2.61	0	10.07	--	NM
23	0.37	3.31	0.05	8.42	--	NM
24	0.25	3.51	0	6.54	--	NM
25	0.01	3.17	0.01	5.86	--	NM
26	0	2.87	0.01	5.46	--	NM
27	0.03	2.33	0.09	5.31	--	NM
28	0	2.52	0.15	5.31	--	NM
29	0	2.93	0	4.83	--	NM
30	0	3.00	0	4.65	--	NM
31	--	--	0	4.32	--	NM
Totals	2.02	--	2.25	--	1.26	--

Note: NM = Not Measured

Total Precipitation Received – November 17, 2014 to January 5, 2015	4.57 inches

3.2.1 Trace 14-01: Former Sinkhole Area Well A. Fluorescein Trace

One pound of fluorescein dye mixture containing approximately 75% dye equivalent and 25% diluent was introduced into the inner casing of Well A in the former sinkhole area on November 17, 2014 at 1315 hours. Approximately 1,524 gallons of water from the deep well on-Site had been discharged into Well A in the 4 hours prior to the dye introduction. The powdered fluorescein dye was mixed with one gallon of water and two gallons of clean water were used to rinse the carboy and well casing. Approximately 7,272 gallons of clean water were added following the dye introduction at a rate of approximately 12 gpm to flush the dye into the groundwater system.

Fluorescein dye from Trace 14-01 was detected in samples collected from New Cricket Spring. Dye from this trace was not detected in Cricket Spring or any sampling stations in the Walnut Creek watershed (including the Railroad Tunnel Spring drainage). Small concentrations of fluorescein were detectable at the discharge from Cricket Pond- (maximum if 159 ppb on 12/2/14) and in certain on-Site wells adjacent to the former sinkhole. The Cricket Pond station receives water that has discharged from New Cricket Spring and then been treated with ozone prior to discharge to the Cricket Creek channel. Data from all sampling stations are provided in Appendix B. Table 9 summarizes the results from activated carbon samplers and grab water samples from New Cricket Spring.

Table 9. Fluorescein Results From Activated Carbon and Grab Water Samples at Station 1, New Cricket Spring, for Trace 14-01.

Sampling Period	Peak Emission Wavelength in Activated Carbon (nm)	Fluorescein Concentration		
		Total in Activated Carbon (ppb)	Mean Concentration per Day (ppb/day)	Corresponding Water Sample (ppb)
11/07/14 to 11/17/14	516.0 *	3.68	0.369	ND
11/17/14 at 13:15 hrs	Fluorescein Dye Introduction			
11/17/14 to 11/18/14	516.3	43,000	34,700	748
11/18/14 to 11/24/14	516.2	61,300	10,500	173
11/24/14 to 12/02/14	516.5	11,600	1,460	47.7
12/02/14 to 12/08/14	516.2	3,220	536	18.1
12/08/14 to 12/15/14	516.1	2,720	387	8.94
12/15/14 to 12/22/14	516.2	638	92	4.50
12/22/14 to 12/29/14	516.2	505	71	3.60
12/29/14 to 01/05/15	516.1	545	78	1.28
01/05/15 to 01/23/15	516.7	208	11	1.86

Notes: ND = Not detected
* Does not meet all criteria for a positive dye detection, but calculated for background purposes.

The results from the activated carbon samplers (mean concentration per day) and the corresponding grab samples of water indicate the dye pulse peaked within the first day following the dye introduction and then rapidly decreased with time in the following weeks.

Additional information can be obtained by reviewing the composite water sample results from the ISCO automatic pump sampler in Appendix B. Table 10 summarizes the composite water samples results and mean flow rates during the first week following the Trace 14-01 dye introduction.

Table 10. Composite Water Sample Results for Fluorescein at Station 1, New Cricket Spring, for the First Week Following Dye Introduction, for Trace 14-01.

Composite Water Sample Period		Composite Water Sample Results		Mean Flow Rate During Composite Sample Period (gpm)
Beginning	Ending	Peak Emission Wavelength (nm)	Fluorescein Concentration (ppb)	
11/17/2014 at 1315 hours		Fluorescein dye introduction		
11/17/14 1300	11/17/14 2000	507.3	375	4.59
11/17/14 2100	11/18/14 0400	507.3	4,300	8.36
11/18/14 0500	11/18/14 1200	507.3	1,030	10.01
11/18/14 1300	11/18/14 2000	507.5	707	8.68
11/18/14 2100	11/19/14 0400	507.5	1,330	5.98
11/19/14 0500	11/19/14 1200	507.5	1,750	3.89
11/19/14 1300	11/19/14 2000	507.7	2,160	3.24
11/19/14 2100	11/20/14 0400	507.6	1,890	2.63
11/20/14 0500	11/20/14 1200	507.4	1,290	2.43
11/20/14 1300	11/20/14 2000	507.5	1,020	2.19
11/20/14 2100	11/21/14 0400	507.4	768	2.31
11/21/14 0500	11/21/14 1200	507.5	638	2.50
11/21/14 1300	11/21/14 2000	507.4	461	2.40
11/21/14 2100	11/22/14 0400	507.3	448	2.31
11/22/14 0500	11/22/14 1200	507.6	339	2.43
11/22/14 1300	11/22/14 2000	507.5	304	2.70
11/22/14 2100	11/23/14 0400	507.5	273	3.10
11/23/14 0500	11/23/14 1200	507.4	251	3.33
11/23/14 1300	11/23/14 2000	507.4	210	3.38
11/23/14 2100	11/24/14 0400	507.4	183	3.43
11/24/14 0500	11/24/14 1200	507.3	375	3.54

The first arrival of fluorescein dye from Trace 14-01 occurred in the composite sample collected from 11/17/14 at 1300 to 11/17/14 at 2000 with a concentration of 375 ppb. Based upon periodic grab samples of water collected from the spring for several hours after the dye introduction, the first arrival of the dye occurred after 11/17/14 at 1715 and before 11/17/14 at 2000 (4 to 8 hours after dye introduction). The maximum dye concentration occurred between 11/17/14 at 2100 hours

and 11/18/14 at 0400 hours (8 to 16 hours after the dye introduction) as the flow rate from the spring was increasing due to the clean water introduced to flush the dye into the groundwater system.

3.2.2 Trace 14-02: Former Sinkhole Area Well B Trace

Four pounds of rhodamine WT dye mixture containing approximately 20% dye equivalent and 80% diluent was introduced into the inner casing of Well B in the former sinkhole area on November 17, 2014 at 1308 hours. Approximately 1,524 gallons of water from the deep well on-Site had been discharged into the well in the 4 hours prior to the dye introduction. Two gallons of clean water were used to rinse the dye container and well casing. Approximately 7,272 gallons of clean water, at a rate of approximately 12 gpm, were added following the dye introduction.

Rhodamine WT dye from Trace 14-02 was detected in samples from New Cricket Spring. Dye from this trace was not detected in Cricket Spring or any sampling stations in the Walnut Creek watershed (including the Railroad Tunnel Spring drainage). Small concentrations of rhodamine WT were detectable at the discharge from Cricket Pond –(maximum of 27.8 ppb on 12/2/14) and in certain on-Site wells adjacent to the former sinkhole. The Cricket Pond station receives water that has discharged from New Cricket Spring and then been treated with ozone prior to discharge to the Cricket Creek channel. Data from all sampling stations are provided in Appendix B. Table 11 summarizes the rhodamine WT results from activated carbon samplers and grab water samples from New Cricket Spring.

Table 11. Rhodamine WT Results From Activated Carbon and Grab Water Samples at Station 1, New Cricket Spring for Trace 14-02.

Sampling Period	Peak Emission Wavelength in Activated Carbon (nm)	Rhodamine WT Concentration		
		Total in Activated Carbon (ppb)	Mean Concentration per Day (ppb/day)	Corresponding Water Sample (ppb)
11/07/14 to 11/17/14	ND	--	--	ND
11/17/14 at 13:08	Rhodamine WT Dye Introduction			
11/17/14 to 11/18/14	567.0	111,000	89,500	3,320
11/18/14 to 11/24/14	567.3	204,000	35,000	553
11/24/14 to 12/02/14	567.5	34,000	4,270	162
12/02/14 to 12/08/14	567.5	9,490	1,580	72.3
12/08/14 to 12/15/14	567.8	8,910	1,270	38.6
12/15/14 to 12/22/14	567.8	3,700	534	22.6
12/22/14 to 12/29/14	568.4	3,370	475	23.7
12/29/14 to 01/05/15	567.6	3,270	467	9.42
01/05/15 to 01/23/15	568.9	2,350	130	14.3

Notes: ND = Not detected

Both the results from the activated carbon samplers (mean concentration per day) and the corresponding grab samples of water indicate the dye pulse peaked within the first day following the

dye introduction and then rapidly decreased in the following weeks. This trend was also observed with the fluorescein dye in Trace 14-01.

Additional information can be obtained by reviewing the composite water samples collected by the ISCO automatic pump sampler (see Appendix B). Table 12 summarizes composite water sample results and mean flow rates during the first week following the Trace 14-02 dye introduction.

Table 12. Composite Water Sample Results for Rhodamine WT at Station 1, New Cricket Spring, for the First Week Following Dye Introduction for Trace 14-02.

Composite Water Sample Period		Composite Water Sample Results		Mean Flow Rate During Composite Sample Period (gpm)
Beginning	Ending	Peak Emission Wavelength (nm)	Rhodamine WT Concentration (ppb)	
11/17/2014 at 1308 hours		Rhodamine WT dye introduction		
11/17/14 1300	11/17/14 2000	574.2	1,100	4.59
11/17/14 2100	11/18/14 0400	574.2	14,500	8.36
11/18/14 0500	11/18/14 1200	574.3	4,360	10.01
11/18/14 1300	11/18/14 2000	574.1	2,760	8.68
11/18/14 2100	11/19/14 0400	574.2	4,460	5.98
11/19/14 0500	11/19/14 1200	574.1	5,110	3.89
11/19/14 1300	11/19/14 2000	574.2	6,180	3.24
11/19/14 2100	11/20/14 0400	574.1	4,790	2.63
11/20/14 0500	11/20/14 1200	574.2	3,640	2.43
11/20/14 1300	11/20/14 2000	574.1	2,820	2.19
11/20/14 2100	11/21/14 0400	574.1	2,260	2.31
11/21/14 0500	11/21/14 1200	574.1	1,880	2.50
11/21/14 1300	11/21/14 2000	574.2	1,400	2.40
11/21/14 2100	11/22/14 0400	574.1	1,415	2.31
11/22/14 0500	11/22/14 1200	574.6	1,080	2.43
11/22/14 1300	11/22/14 2000	574.4	1,030	2.70
11/22/14 2100	11/23/14 0400	574.5	941	3.10
11/23/14 0500	11/23/14 1200	574.5	886	3.33
11/23/14 1300	11/23/14 2000	574.5	713	3.38
11/23/14 2100	11/24/14 0400	574.3	658	3.43
11/24/14 0500	11/24/14 1200	574.2	1,100	3.54

The first arrival of rhodamine WT dye from Trace 14-02 occurred in the composite sample collected from 11/17/14 at 1300 to 11/17/14 at 2000 at a concentration of 1,100 ppb. Based upon periodic grab samples of water collected from the spring for several hours after the dye introduction, the first arrival of the dye occurred after 11/17/14 at 1715 and before 11/17/14 at 2000 (4 to 8 hours after dye introduction). The maximum dye concentration occurred between 11/17/14 at 2100 hours and 11/18/14 at 0400 hours (8 to 16 hours after dye introduction) as the flow rate from the spring

was increasing due to the clean water introduced to flush the dye into the groundwater system. This is the same time period that the peak concentration from the fluorescein trace was observed.

3.3 Calculations

Quality control and mass balance calculations were performed on data collected during the groundwater tracer study. These calculations are discussed in this section. Calculations are presented in Appendix C.

3.3.1 Quality Control Calculations

Duplicate samples were analyzed for all activated carbon samplers collected at New Cricket Spring. The mean and relative percent difference (RPD) was calculated for each of these duplicate samples. RPD equals the difference between a value and its duplicate or replicate divided by the mean of the two values. The calculated values are shown in Table C-1 in Appendix C. A summary of the RPD values is shown in Table 13.

Table 13. Relative Percent Difference Values for Activated Carbon Samplers.

Dye in Carbon Samplers	Range of RPD Values	Mean RPD
Fluorescein	1.2% to 51.9%	16.5%
Rhodamine WT	6.4% to 32.6%	15.7%

The highest RPD value (51.9% for fluorescein and 32.6% for rhodamine WT) was from a sample where one of the two samplers was moved out of the spring branch during a high flow event. The mean RPD calculated without this outlier is 12.5% for fluorescein and 13.6% for rhodamine WT.

Replicate water samples were analyzed for selected composite water samples collected with the ISCO automatic pump samplers at New Cricket Spring. The mean and RPD for each of these replicate samples is presented in Table C-2 in Appendix C. A summary of the RPD values is shown in Table 14.

Table 14. Relative Percent Difference Values for Composite Water Samples.

Dye in Water Samples	Range of RPD Values	Mean RPD
Fluorescein	0% to 9.9%	1.8%
Rhodamine WT	0.1% to 9.9%	2.8%

The RPD values of both the activated carbon duplicate samples and the composite water replicate samples are within acceptable ranges for OUL standard laboratory quality control for the analysis of fluorescent tracer dyes.

3.3.2 Mass Balance Calculations

The mass of dye discharging from New Cricket Spring was calculated from the composite water samples and flow rate measurements. The mass of the each dye discharged from the spring was calculated by multiplying the concentration of the composite water sample by the flow rate from the spring during the sampling period. When replicate water samples were analyzed, the mean concentration was used in the calculation. Flow was calculated using the mean flow rate for the sampling period based upon hourly flow rate measurements recorded by the pressure transducer. The mean flow rate was then multiplied by the length of the time period to determine the total flow for each time period. The calculations are presented in Table C-3 in Appendix C. A summary of the mass calculations is shown in Table 15.

Table 15. Mass Balance for the Tracer Dyes Detected During the Study Period.

Parameter	Fluorescein	Rhodamine WT
Total Mass Detected	205 grams	686 grams
	0.45 pounds	1.51 pounds
Initial Mass of Dye Introduced	1 pound	4 pounds
Percentage Detected in Water from New Cricket Spring	45%	38%

The technical literature suggests that dye traces from sinkholes to springs are typically characterized by 20 to 50% of the introduced dye being detected at the receiving spring (Aley 1997). The detection percentages from this study are within the reported range. The recovery percent was greater for fluorescein than rhodamine WT. There are two possible explanations for this. First, rhodamine WT has a greater sorption tendency onto aquifer materials than fluorescein. Second, even though the two wells used for dye introduction are only about 23 feet apart, subsurface conditions in the vicinity of the two wells may have been different.

Mobile porosity is the percent of total porosity that is actually transporting the majority of groundwater (Sutherson et al. 2014). As noted earlier, a default estimate for mobile porosity in regulatory guidance is 20%. The detection percents for the two dye traces (45% for fluorescein and 38% for rhodamine WT) provide a measure of mobile porosity in the most contaminated portion of the groundwater system at the Arkwood Site. None of the introduced tracer dyes were detected at any other sampling station except minor amounts at Cricket Pond and in certain on-Site wells adjacent to the former sinkhole. As a result, the remainder of the introduced dye (55% of the fluorescein and 62% of the rhodamine WT) has been detained within the non-mobile portion of the epikarstic aquifer. Detainment of contaminants of concern has also occurred within the same portion of the epikarstic aquifer and represents the primary source of contaminants that continue to discharge from New Cricket Spring and are being treated at the water treatment system located adjacent to that spring.

Table 16 summarizes travel times for the first arrival of each dye, the peak arrival, and the times for 50% and 90% of the detected dyes to reach New Cricket Spring.

Table 16. Important Travel Times for Dyes Discharging from New Cricket Spring.

Parameter	Fluorescein	Rhodamine WT
First arrival of dye	4 to 8 hours	4 to 8 hours
Arrival of Peak Concentration	8 to 16 hours	8 to 16 hours
Time for 50% of dye detected to arrive at spring	Less than 39 hours	Less than 39 hours
Time for 90% of dye detected to arrive at spring	Less than 287 hours (almost 12 days)	Less than 443 hours (over 18 days)

The duration of the regular sampling events following the dye introduction was 7 weeks (1,176 hours). The first arrival of both dyes occurred between 4 and 8 hours after dye introduction. The arrival time for the maximum dye concentrations for both dyes occurred 8 to 16 hours following the dye introduction (approximately half a day). The time for 50% of the detected dye to arrive at New Cricket Spring occurred for both dyes at less than 39 hours, or slightly more than a day and a half after dye introduction. The time for 90% of the detected dye to arrive at the spring was different for the two dyes. The time for 90% of the detected fluorescein dye to arrive at the spring occurred in less than 287 hours, or almost 12 days. For the rhodamine WT, the time for 90% of the detected dye to arrive at the spring was less than 443 hours, or just over 18 days. One possible explanation for the travel time difference is that fluorescein is a more conservative tracer dye, and as such the bulk of the dye pulse may have moved through the groundwater system more rapidly than the rhodamine WT. Since the designed study period was 49 days (7 weeks) in length, and 90% of the detected dye discharged from New Cricket Spring within 12 to 18 days, the sampling duration was clearly adequate for the purposes of this study.

4 SUMMARY AND CONCLUSIONS

A supplemental groundwater tracing study was conducted to quantify groundwater flow paths from the former sinkhole area at the Arkwood, Inc. Superfund Site to New Cricket Spring. The study was part of ongoing groundwater remediation activities at the Site.

Two groundwater traces were performed as part of this study. The two dye introduction wells are about 22 feet apart and both bottom in the epikarstic zone.

- **Trace 14-01: Former Sinkhole Area Well A Trace.** One pound of fluorescein dye mixture was introduced into Well A near the former sinkhole at the Site. Dye from this trace was detected in New Cricket Spring. Dye was not detected in Cricket Spring, the two Railroad Tunnel Spring discharges, or in the Walnut Creek valley.

- **Trace 14-02: Former Sinkhole Area Well B Trace.** Four pounds of rhodamine WT dye mixture was introduced into Well B near the former sinkhole at the Site. Dye from this trace was detected in New Cricket Spring. Dye was not detected in Cricket Spring, the two Railroad Tunnel Spring discharges, or in the Walnut Creek valley.

Important conclusions from the study are as follows:

1. Groundwater from the former sinkhole area on-Site only discharges from New Cricket Spring. Groundwater from this area does not discharge from Cricket Spring, the southeast end of the railroad tunnel, or in the Walnut Creek valley.

2. Both dyes first arrived at New Cricket Spring 4 to 8 hours after the dye introductions. The arrival of the maximum concentrations of both dyes occurred 8 to 16 hours after the dye introductions.

3. Ninety percent of the detected fluorescein dye discharged from New Cricket Spring within about 12 days after dye introduction. Ninety percent of the detected rhodamine WT dye discharged from New Cricket Spring within about 18 days after dye introduction. Based on water samples, the concentrations of both dyes had declined by over three orders of magnitude by the end of sampling, which occurred seven weeks after dye introduction. This was the sampling duration specified in the Work Plan for the study, and it was clearly an adequate duration of sampling.

4. The total mass of fluorescein dye detected at New Cricket Spring was 205 grams (45% of the introduced dye). The total mass of rhodamine WT dye detected at this station was 686 grams (38% of the introduced dye). These values are within the expected detection range of 20% to 50% for dye traces from sinkholes to springs (Aley 1997 and 2014).

5. The percent of dye detected at New Cricket Spring (45% for fluorescein and 38% for rhodamine WT) provides a measure of mobile porosity for the contaminated portion of the epikarstic aquifer lying between the former sinkhole area and New Cricket Spring. It is the conclusion of the OUL that the larger value (45%) is the better value for mobile porosity since rhodamine WT is subject to relatively greater adsorption losses onto earth materials.

6. A common default value for the percent of mobile porosity in aquifers is 20% (Sutherson et al. 2014). The remaining 80% of total porosity is non-mobile. Based on dye tracing results the non-mobile porosity in the tested portion of the epikarstic aquifer at the Arkwood site is 55%. Given these values, and the absence of dye detections at off-site locations (except minor detections at Cricket Pond), the data clearly demonstrate that the introduced dyes either discharged from New Cricket Spring or are detained within the non-mobile porosity of the epikarstic aquifer associated with the former sinkhole area on-Site and New Cricket Spring.

7. 55% of the introduced fluorescein and 62% of the introduced rhodamine WT did not discharge from New Cricket Spring during the seven-week study period. It is the conclusion of the OUL that these dyes are detained in the non-mobile portion of the epikarstic aquifer in the segment of this aquifer between the former sinkhole area on-Site and New Cricket Spring.

8. Mean RPD values for duplicate activated carbon samplers ranged from 15.7% to 16.5%. Mean RPD values for replicate water sample ranged from 2.1 to 2.9%. These values demonstrate that the semi-quantitative measurements are of good quality.

5 REFERENCES

Aley, Thomas. 1992. Final report; groundwater tracing investigation, Arkwood Inc. Site, Omaha, Arkansas. Vol. 1 text 84p. plus Appendix A (tables of results) 103p. Vol. 2. Analytical graphs, no page numbers.

Aley, Thomas. 1997. Groundwater tracing in the epikarst. IN: Proc. 6th Multidisciplinary Conference on Sinkholes and Hydrogeology of Karst Terranes. The Engineering Geology and Hydrogeology of Karst Terranes. A.A Balkema, Rotterdam, pp. 207-211.

Aley, Thomas. 2014. Revised final supplemental groundwater tracing study work plan Arkwood Superfund Site, Omaha, Arkansas. Ozark Underground Laboratory contract report for McKesson Corporation, San Francisco. 8p. + attachments.

Aley, Thomas and Shiloh Kirkland. 2011. Procedures and criteria for the analysis of fluorescent dyes in water and charcoal samplers: fluorescein, eosine, rhodamine WT, and sulforhodamine B dyes. Ozark Underground Laboratory, Inc. September 1, 2012. 19 p.

Field, Malcolm S, R.G. Wilhelm, J.F. Quinlan, and T.J. Aley. 1995. An assessment of the potential adverse properties of fluorescent tracer dyes used for groundwater tracing. *Environmental Monitoring and Assessment*, Vol.38, pp. 75-96. Kluwar Academic Publishers.

Smart, P.L. 1984. A review of the toxicity of twelve fluorescent dyes used for water tracing. National Speleological Society Bulletin, Vol. 46, pp. 21-33.

Sutherson, Suthan; Craig Devine; Elizabeth Cohen; and Kim Heinze. 2014. Tracer testing: recommended best practice for design and optimization of *in situ* remediation systems. Groundwater Monitoring and Remediation, National Ground Water Association, Vol. 34:3, pp. 33-40.

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APPENDIX A

Ozark Underground Laboratory's
Procedures and Criteria Document

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PROCEDURES AND CRITERIA
ANALYSIS OF FLUORESCENT DYES
IN WATER AND CHARCOAL SAMPLERS:

FLUORESCEIN, EOSINE, RHODAMINE WT, AND SULFORHODAMINE B DYES

Revision Date:
September 1, 2011

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INTRODUCTION

This document describes standard procedures and criteria currently in use at the Ozark Underground Laboratory (OUL) as of the date shown on the title page. Some samples may be subjected to different procedures and criteria because of unique conditions; such non-standard procedures and criteria are identified in reports for those samples. Standard procedures and criteria change as knowledge and experience increases and as equipment is improved or up-graded. The OUL maintains a summary of changes in standard procedures and criteria.

TRACER DYES AND SAMPLE TYPES

Dye Nomenclature

Dye manufacturers and retailers use a myriad of names for the dyes. This causes confusion among dye users and report readers. The primary dyes used at the OUL and described in this document are included in Table 1 below.

Table 1. Primary OUL Dye Nomenclature.

OUL Common Name	Color Index Number	Color Index Name	Other Names
Fluorescein	45350	Acid Yellow 73	uranine, uranine C, sodium fluorescein, fluorescein LT and fluorescent yellow/green
Eosine	45380	Acid Red 87	eosin, eosine OJ, and D&C Red 22
Rhodamine WT	None assigned	Acid Red 388	fluorescent red (but not the same as rhodamine B)
Sulforhodamine B	45100	Acid Red 52	pontacyl brilliant pink B, lissamine red 4B, and fluoro brilliant pink

The OUL routinely provides dye for tracing projects. Dyes purchased for groundwater tracing are always mixtures that contain both dye and an associated diluent. Diluents enable the manufacturer to standardize the dye mixture so that there are minimal differences among batches. Additionally, diluents are often designed to make it easier to dissolve the dye mixture in water, or to produce a product which meets a particular market need (groundwater tracing is only a tiny fraction of the dye market). The percent of dye in “as-sold” dye mixtures often varies dramatically among manufacturers and retailers, and retailers are sometimes incorrect about the percent of dye in their products. The OUL subjects all of its dyes to strict quality control (QC) testing. Table 2 summarizes the as-sold dye mixtures used by the OUL.

Table 2. As-Sold Dye Mixtures at the OUL.

OUL Common Name	Form	Dye Equivalent
Fluorescein	Powder	75% dye equivalent, 25% diluent
Eosine	Powder	75% dye equivalent, 25% diluent
Rhodamine WT	Liquid	20% dye equivalent, 80% diluent
Sulforhodamine B	Powder	75% dye equivalent, 25% diluent

Analytical results are based on the as-sold weights of the dyes provided by the OUL. The use of dyes from other sources is discouraged due to the wide variability of dye equivalents within the market. However, if alternate source dyes are used, a sample should be provided to the OUL for quality control and to determine if a correction factor is necessary for the analytical results.

Types of Samples

Typical samples that are collected for fluorescent tracer dye analysis include charcoal samplers (also called activated carbon or charcoal packets) and water samples.

The charcoal samplers are packets of fiberglass screening partially filled with 4.25 grams of activated coconut charcoal. The charcoal used by the OUL is Calgon 207C coconut shell carbon, 6 to 12 mesh, or equivalent. The most commonly used charcoal samplers are about 4 inches long by 2 inches wide. A cigar-shaped sampler is made for use in very small diameter wells (such as 1-inch diameter piezometers); this is a special order item and should be specifically requested in advance when needed. All of the samplers are closed by heat sealing.

In specialized projects, soil samples have been collected from soil cores and analyzed for fluorescent tracer dyes. Project-specific procedures have been developed for projects such as these. For additional information, please contact the OUL.

FIELD PROCEDURES

Field procedures included in this section are intended as guidance, and not firm requirements. Placement of samplers and other field procedures require adjustment to field conditions. Personnel at the OUL are available to provide additional assistance for implementation of field procedures specific to specialized field conditions.

Placement of Samplers

Charcoal samplers are placed so as to be exposed to as much water as possible. Water should flow through the packet. In springs and streams they are typically attached to a rock or other anchor in a riffle area. Attachment of the packets often uses plastic tie wires. In swifter water galvanized wire (such as electric fence wire) is often used. Other types of anchoring wire can be used. Electrical wire with plastic insulation is also good. Packets are attached so that they extend outward from the anchor rather than laying flat against it. Two or more separately

anchored packets are typically used for sampling springs and streams. The placement of multiple packets is recommended in order to minimize the chance of loss during the sampling period. The use of fewer packets is discouraged except when the spring or stream is so small that there is not appropriate space for placing multiple packets.

When pumping wells are being sampled, the samplers are typically placed in sample holders made of plastic pipe fittings. Brass hose fittings can be at the end of the sample holders so that the sample holders can be installed on outside hose bibs and water which has run through the samplers can be directed to waste through a connected garden hose. The samplers can be unscrewed in the middle so that charcoal packets can be changed. The middle portions of the samplers consist of 1.5 inch diameter pipe and pipe fitting.

Charcoal packets can be lowered into monitoring wells for sampling purposes. In general, if the well is screened, samplers should be placed approximately in the middle of the screened interval. Due to the typically lower volume of water that flows through a well, only one charcoal sampler should be used per well. However, multiple packets can be placed in a single well at depths to test different depth horizons when desirable. A weight should be added near the charcoal packet to ensure that it will not float. The weight should be of such a nature that it will not affect water quality. One common approach is to anchor the packets with a white or uncolored plastic cable tie to the top of a dedicated weighted disposable bailer. We typically run nylon cord from the top of the well to the charcoal packet and its weight. ***Do not use colored cord*** since some of them are colored with fluorescent dyes. Nylon fishing line should not be used since it can be readily cut by a sharp projection in the well.

In some cases, especially with small diameter wells and appreciable well depths, the weighted disposable bailers sink very slowly or may even fail to sink because of friction and floating of the anchoring cord. In such cases a weight may be added to the top of the disposable bailer. Stainless steel weights are ideal, but are not needed in all cases. All weights should be cleaned prior to use; the cleaning approach should comply with decontamination procedures in use at the project site.

Optional Preparation of Charcoal Samplers

Charcoal packets routinely contain some fine powder that washes off rapidly when they are placed in water. While not usually necessary, the following optional preparation step is suggested if the fine charcoal powder is problematic.

Charcoal packets can be triple rinsed with distilled, demineralized, or reagent water known to be free of tracer dyes. This rinsing is typically done by soaking. With this approach, approximately 25 packets are placed in one gallon of water and soaked for at least 10 minutes. The packets are then removed from the water and excess water is shaken off the packets. The packets are then placed in a second gallon of water and again soaked for at least 10 minutes. After this soaking they are removed from the water and excess water is shaken off the packets. The packets are then placed in a third gallon of water and the procedure is again repeated. Rinsed packets are placed in plastic bags and are placed at sampling stations within three days. Packets can also be rinsed in jets of water for about one minute; this requires more water and is typically difficult to do in the field with water known to be free of tracer dyes.

Collection and Replacement of Samplers

Samplers are routinely collected and replaced at each of the sampling stations. The frequency of sampler collection and replacement is determined by the nature of the study. Collections at one week intervals are common, but shorter or longer collection frequencies are acceptable and sometimes more appropriate. Shorter sampling frequencies are often used in the early phases of a study to better characterize time of travel. As an illustration, we often collect and change charcoal packets 1, 2, 4, and 7 days after dye injection. Subsequent sampling is then weekly.

The sampling interval in wells at hazardous wastes sites should generally be no longer than about a week. Contaminants in the water can sometimes use up sorption sites on the charcoal that would otherwise adsorb the dye. This is especially important if the dye might pass in a relatively short duration pulse.

Where convenient, the collected samplers should be briefly rinsed in the water being sampled to remove dirt and accumulated organic material. This is not necessary with well samples. The packets are shaken to remove excess water. Next, the packet (or packets) are placed in a plastic bag (Whirl-Pak® bags are ideal). The bag is labeled on the outside with a black permanent type felt marker pen, such as a Sharpie®. ***Use only pens that have black ink***; colored inks may contain fluorescent dyes. The notations include station name or number and the date and time of collection. Labels must not be inserted inside the sample bags.

Collected samplers are kept in the dark to minimize algal growth on the charcoal prior to analysis work. New charcoal samplers are routinely placed when used charcoal packets are collected. The last set of samplers placed at a stream or spring is commonly not collected.

Water Samples

Water samples are often collected. They should be collected in either glass or plastic; the OUL routinely uses 50 milliliter (mL) research-grade polypropylene copolymer Perfector Scientific vials (Catalog Number 2650) for such water samples. No more than 30 mL of water is required for analysis. The sides of the vials should be labeled with the project name, sample ID, sample date and time with a black permanent felt tip pen. ***Do not label the lid only***. The vials should be placed in the dark and refrigerated immediately after collection, and maintained under refrigeration until shipment. The OUL supplies vials for the collection of water samples.

Sample Shipment

When water or charcoal samplers are collected for shipment to the OUL they should be shipped promptly. We prefer (and in some studies require) that samples be refrigerated with frozen re-usable ice packs upon collection and that they be shipped refrigerated with frozen ice packs by overnight express. ***Do not ship samplers packed in wet ice*** since this can create a potential for cross contamination when the ice melts. Our experience indicates that it is not essential for samplers to be maintained under refrigeration; yet maintaining them under refrigeration clearly minimizes some potential problems. A product known as "green ice" should not be used for maintaining the samples in a refrigerated condition since this product contains a dye which could contaminate samples if the "green ice" container were to break or leak.

We receive good overnight and second day air service from both UPS and FedEx. The U.S. Postal Service does not typically provide next day service to us. DHL does not provide

overnight service to us. FedEx is recommended for international shipments. The OUL does not receive Saturday delivery.

Each shipment of charcoal samplers or water samples ***must be accompanied by a sample custody document***. The OUL provides a sheet (which bears the title "Samples for Fluorescence Analysis") that can be used if desired. These sheets can be augmented by a client's chain-of-custody forms or any other relevant documentation. OUL's custody document works well for charcoal samplers because it allows for both the placement date and time as well as the collection date and time. Many other standard chain-of-custody documents do not allow for these types of samples. Attachment 1 includes a copy of OUL's Sample Collection Data Sheet.

Please write legibly on the custody documents and ***use black ink***. Check the accuracy of the sample sheet against the samples prior to shipment to identify and correct errors that may delay the analysis of your samples following receipt at the laboratory.

Supplies Provided by the OUL

The OUL provides supplies for the collection of fluorescent tracer dyes. Supplies provided upon request are charcoal packets, Whirl-Pak® bags (to contain the charcoal packets after collection for shipment to the laboratory), and water vials. These supplies are subjected to strict QA/QC procedures to ensure the materials are free of any potential tracer dye contaminants. The charge for these materials is included in the cost of sample analysis. Upon request, coolers and re-freezable ice packs are also provided for return shipment of samples.

The OUL also has tracer dyes available for purchase. These dyes are subject to strict QA/QC testing. All analytical work is based upon the OUL as-sold weight of the dyes.

LABORATORY PROCEDURES

The following procedures are followed upon receipt of samples at the laboratory.

Receipt of Samples

Samplers shipped to the OUL are logged in and refrigerated upon receipt. Prior to cleaning and analysis, samplers are assigned a laboratory identification number.

It sometimes occurs that there are discrepancies between the sample collection data sheet and the actual samples received. When this occurs, a "Discrepancy Sheet" form is completed and sent to the shipper of the sample for resolution. The purpose of the form is to help resolve discrepancies, even when they may be minor. Many discrepancies arise from illegible custody documents. ***Please write legibly*** on the custody documents and ***use black ink***. Check the accuracy of the sample sheet against the samples prior to shipment to identify and correct errors that may delay the analysis of your samples following receipt at the laboratory.

Cleaning of Charcoal Samplers

Samplers are cleaned by spraying them with jets of clean water from a laboratory well in a carbonate aquifer. OUL uses non-chlorinated water for the cleansing to minimize dye deterioration. We do not wash samplers in public water supplies. Effective cleansing cannot generally be accomplished simply by washing in a conventional laboratory sink even if the sink is equipped with a spray unit.

The duration of packet washing depends upon the condition of the sampler. Very clean samplers may require less than a minute of washing; dirtier samplers may require several minutes of washing.

Elution of the Charcoal

There are various eluting solutions that can be used for the recovery of tracer dyes. The solutions typically include an alcohol, water, and a strong basic solution such as aqueous ammonia and /or potassium hydroxide.

The standard elution solution used at the OUL is a mixture of 5% aqua ammonia and 95% isopropyl alcohol solution and sufficient potassium hydroxide pellets to saturate the solution. The isopropyl alcohol solution is 70% alcohol and 30% water. The aqua ammonia solution is 29% ammonia. The potassium hydroxide is added until a super-saturated layer is visible in the bottom of the container. This super-saturated layer is not used for elution. Preparation of eluting solutions uses dedicated glassware which is never used in contact with dyes or dye solutions.

The eluting solution will elute fluorescein, eosine, rhodamine WT, and sulforhodamine B dyes. It is also suitable for separating fluorescein peaks from peaks of some naturally present materials found in may be found in samplers.

Fifteen mL of the eluting solution is poured over the washed charcoal in a disposable sample beaker. The sample beaker is capped. The sample is allowed to stand for 60 minutes. After this time, the liquid is carefully poured off the charcoal into a new disposable beaker which has been appropriately labeled with the laboratory identification number. A few grains of charcoal may inadvertently pass into the second beaker; no attempt is made to remove these from the second sample beaker. After the pouring, a small amount of the elutant will remain in the initial sample beaker. After the transfer of the elutant to the second sample beaker, the contents of the first sample beaker (the eluted charcoal) are discarded. Samples are kept refrigerated until analyzed.

pH Adjustment of Water Samples

The fluorescence intensity of several of the commonly used fluorescent tracer dyes is pH dependent. The pH of samples analyzed for fluorescein, eosine, and pyranine dyes are adjust to a target pH of greater than 9.5 in order to obtain maximum fluorescence intensities.

Adjustment of pH is achieved by placing samples in a high ammonia atmosphere for at least two hours in order to increase the pH of the sample. Reagent water standards are placed in the same atmosphere as the samples. If dye concentrations in a sample are off-scale and require

dilution for quantification of the dye concentration, the diluting water used is OUL reagent water that has been pH adjusted in a high ammonia atmosphere. Samples that are only analyzed for rhodamine WT or sulforhodamine B are not required to be pH adjusted.

Analysis on the Shimadzu RF-5301

The OUL uses a Shimadzu spectrofluorophotometer model RF-5301. This instrument is capable of synchronous scanning. The OUL also owns a Shimadzu RF-540 spectrofluorometers that is occasionally used for special purposes.

A sample of the elutant or water is withdrawn from the sample container using a disposable polyethylene pipette. Approximately 3 mL of the sample is then placed in disposable rectangular polystyrene cuvette. The cuvette has a maximum capacity of 3.5 mL. The cuvette is designed for fluorometric analysis; all four sides and the bottom are clear. The acceptable spectral range of these cuvettes is 340 to 800 nm. The pipettes and cuvettes are discarded after one use.

The cuvette is then placed in the RF-5301. This instrument is controlled by a programmable computer and operated by proprietary software developed for dye tracing applications.

Our instruments are operated and maintained in accordance with the manufacturer's recommendations. On-site installation of our first instrument and a training session on its use was provided by the instrument supplier. Repairs are made by a Shimadzu-authorized repairman.

Our typical analysis of an elutant sample where fluorescein, eosine, rhodamine WT, or sulforhodamine B dyes may be present includes synchronous scanning of excitation and emission spectra with a 17 nm separation between excitation and emission wavelengths. For these dyes, the excitation scan is from 443 to 613 nm; the emission scan is from 460 to 630 nm. The emission fluorescence from the scan is plotted on a graph. The typical scan speed setting is “fast” on the RF-5301. The typical sensitivity setting used is "high."

Table 3. Excitation and emission slit width settings routinely used for dye analysis.

Parameter	**Excitation Slit (nm)**	**Emission Slit (nm)**
ES, FL, RWT, and SRB in elutant	3	1.5
ES, FL, RWT, and SRB in water	5	3

Note: ES = Eosine. FL = Fluorescein. RWT = Rhodamine WT. SRB = Sulforhodamine B.

The instrument produces a plot of the synchronous scan for each sample; the plot shows emission fluorescence only. The synchronous scans are subjected to computer peak picks using proprietary software; peaks are picked to the nearest 0.1 nm. Instrument operators have the ability to manually adjust peaks as necessary based upon computer-picked peaks and experience. All samples run on the RF-5301 are stored electronically with sample information. All samples analyzed are recorded in a bound journal.

Quantification

We calculate the magnitude of fluorescence peaks for fluorescein, eosine, rhodamine WT, and sulforhodamine B dyes in both elutant and water samples. Dye quantities are expressed in microgram per liter (parts per billion; ppb). The dye concentrations are calculated by separating fluorescence peaks due to dyes from background fluorescence on the charts, and then calculating the area within the fluorescence peak. This area is proportional to areas obtained from standard solutions.

We run dye concentration standards each day the RF-5301 is used. Six standards are used; the standard or standards appropriate for the analysis work being conducted are selected. All standards are based upon the as-sold weights of the dyes. The standards are as follows:

1) 10 ppb fluorescein and 100 ppb rhodamine WT in well water from the Jefferson City-Cotter Formation
2) 10 ppb eosine in well water from the Jefferson City-Cotter Formation
3) 100 ppb sulforhodamine B in well water from the Jefferson City-Cotter Formation.
4) 10 ppb fluorescein and 100 ppb rhodamine WT in elutant.
5) 10 ppb eosine in elutant.
6) 100 ppb sulforhodamine B in elutant.

Preparation of Standards

Dye standards are prepared as follows:

Step 1. A small sample of the as-sold dye is placed in a pre-weighed sample vial and the vial is again weighed to determine the weight of the dye. We attempt to use a sample weighing between 1 and 5 grams. This sample is then diluted with well water to make a 1% dye solution by weight (based upon the as-sold weight of the dye). The resulting dye solution is allowed to sit for at least four hours to ensure that all dye is fully dissolved.

Step 2. One part of each dye solution from Step 1 is placed in a mixing container with 99 parts of well water. Separate mixtures are made for fluorescein, rhodamine WT, eosine, and sulforhodamine B. The resulting solutions contain 100 mg/L dye (100 parts per million dye mixture). The typical prepared volume of this mixture is appropriate for the sample bottles being used; we commonly prepare about 50 mL of the Step 2 solutions. The dye solution from Step 1 that is used in making the Step 2 solution is withdrawn with a digital Finnpipette which is capable of measuring volumes between 0.200 and 1.000 mL at intervals of 0.005 mL. The calibration certificate with this instrument indicates that the accuracy (in percent) is as follows:

At 0.200 mL, 0.90%

At 0.300 mL, 0.28%

At 1.000 mL, 0.30%

The Step 2 solution is called the long term standard. OUL experience indicates that Step 2 solutions, if kept refrigerated, will not deteriorate appreciably over periods of less than a year. Furthermore, these Step 2 solutions may last substantially longer than one year.

Step 3. A series of intermediate-term dye solutions are made. Approximately 45 mL. of each intermediate-term dye solution is made. All volume measurements of less than 5 mL are made with a digital Finnpipette. (see description in Step 2). All other volume measurements are made with Rheinland Kohn Geprufte Sicherheit 50 mL capacity pump dispenser which will pump within plus or minus 1% of the set value. The following solutions are made; all concentrations are based on the as-sold weight of the dyes:

1) 1 ppm fluorescein dye and 10 ppm rhodamine WT dye.
2) 1 ppm eosine.
3) 10 ppm sulforhodamine B dye.

Step 4. A series of six short-term dye standards are made from solutions in Step 3. These standards were identified earlier in this section. In the experience of the OUL these standards have a useful shelf life in excess of one week. However, in practice, Step 4 elutant standards are made weekly, and Step 4 water standards are made daily.

Dilution of Samples

Samples with peaks that have arbitrary fluorescence unit values of 500 or more are diluted a hundred fold to ensure accurate quantification.

Some water samples have high turbidity or color which interferes with accurate detection and measurement of dye concentrations. It is often possible to dilute these samples and then measure the dye concentration in the diluted sample.

The typical dilutions are either 10 fold (1:10) or 100 fold (1:100). A 1:10 dilution involves combining one part of the test sample with 9 parts of water (if the sample is water) or elutant (if the sample is elutant). A 1:100 dilution involves combining one part of the test sample is combined with 99 parts of water or elutant, based upon the sample media. Typically, 0.300 mL of the test solution is combined with 29.700 mL of water (or elutant as appropriate) to yield a new test solution.

All volume measurements of less than 5 mL are made with a digital Finnpipette. All other volume measurements are made with Rheinland Kohn Geprufte Sicherheit 50 mL capacity pump dispenser which will pump within plus or minus 1% of the set value.

The water used for dilution is from a carbonate aquifer. All dilution water is pH adjusted to greater than pH 9.5 by holding it in open containers in a high ammonia concentration chamber. This adjustment takes a minimum of two hours.

Quality Control

Laboratory blanks are run for every sample where the last two digits of the laboratory numbers are 00, 20, 40, 60, or 80. A charcoal packet is placed in a pumping well sampler and at least 25 gallons of unchlorinated water is passed through the sampler at a rate of about 2.5 gallons per minute. The sampler is then subjected to the same analytical protocol as all other samplers.

System functioning tests of the analytical instruments are conducted in accordance with the manufacturer's recommendations. Spiked samples are also analyzed when appropriate for quality control purposes.

All materials used in sampling and analysis work are routinely analyzed for the presence of any compounds that might create fluorescence peaks in or near the acceptable wavelength ranges for any of the tracer dyes. This testing includes approximately 1% of materials used.

Project specific QA/QC samples may include sample replicates and sample duplicates. A replicate sample is when a single sample is analyzed twice. A sample duplicate is where two samples are collected in a single location and both are analyzed. Sample replicates and duplicates are run for QA/QC purposes upon request of the client. These results are reported in the Certificate of Analysis.

Reports

Sample analysis results are typically reported in a Certificate of Analysis. However, specialized reports are provided in accordance with the needs of the client. Certificates of Analysis typically provide a listing of station number, sample ID, and dye concentrations if detected. Standard data format includes deliverables in MS Excel and Adobe Acrobat (.pdf) format. Hard copy of the data package, and copies of the analytical charts are available upon request.

Work at the OUL is directed by Mr. Thomas Aley. Mr. Aley has 45 years of professional experience in hydrology and hydrogeology. He is certified as a Professional Hydrogeologist (Certificate #11576) by the American Institute of Hydrology and licenced as a Professional Geologist in Missouri, Arkansas, Kentucky, and Alabama. Additional details regarding laboratory qualifications are available upon request.

Waste Disposal

All laboratory wastes are disposed of according to applicable state and federal regulations. Waste elutant and water samples are collected in 15 gallon poly drums and disposed with a certified waste disposal facilityas non-hazardous waste.

In special cases, wastes for a particular project may be segregated and returned to the client upon completion of the project. These projects may have samples that contain contaminants that the client must account for all materials generated and disposed. These situations are managed on a case-by-case basis.

CRITERIA FOR DETERMINATION OF POSITIVE DYE RECOVERIES

Normal Emission Ranges and Detection Limits

The OUL has established normal emission fluorescence wavelength ranges for each of the four dyes described in this document. The normal acceptable range equals mean values plus and minus two standard deviations. These values are derived from actual groundwater tracing studies conducted by the OUL.

The detection limits are based upon concentrations of dye necessary to produce emission fluorescence peaks where the signal to noise ratio is 3. The detection limits are realistic for most field studies since they are based upon results from actual field samples rather than being based

upon values from spiked samples in a matrix of reagent water or the elutants from unused activated carbon samplers. In some cases detection limits may be smaller than reported if the water being sampled has very little fluorescent material in it. In some cases detection limits may be greater than reported; this most commonly occurs if the sample is turbid due to suspended material or a coloring agent such as tannic compounds. Turbid samples are typically allowed to settle, centrifuged, or, if these steps are not effective, diluted prior to analysis.

Table 4 provides normal emission wavelength ranges and detection limits for the four dyes when analyzed on the OUL's RF-5301.

Table 4. RF-5301 Spectrofluorophotometer. Normal emission wavelength ranges and detection limits for fluorescein, eosine, rhodamine WT, and sulforhodamine B dyes in water and elutant samples.

Fluorescent Dye	**Normal Acceptable Emission Wavelength Range (nm)**		**Detection Limit (ppb)**	
	Elutant	**Water**	**Elutant**	**Water**
Eosine	540.0 to 545.8	532.8 to 537.3	0.050	0.015
Fluorescein	514.5 to 519.6	506.8 to 510.6	0.025	0.002
Rhodamine WT	565.2 to 571.8	572.4 to 577.7	0.170	0.015
Sulforhodamine B	576.4 to 583.2	580.8 to 584.4	0.080	0.008

Note: Detection limits are based upon the as-sold weight of the dye mixtures normally used by the OUL.
Fluorescein and eosine detection limits in water are based on samples pH adjusted to greater than 9.5.

It is important to note that the normal acceptable emission wavelength ranges are subject to change based on instrument maintenance, a change in instrumentation, or slight changes in dye formulation. Significant changes in normal acceptable emission wavelength ranges will be updated in this document as they occur.

Fluorescence Background

Due to the nature of fluorescence analysis, it is important to identify and characterize any potential background fluorescence at dye introduction and monitoring locations prior to the introduction of any tracer dyes.

There is generally little or no detectable fluorescence background in or near the general range of eosine, rhodamine WT, and sulforhodamine B dyes encountered in most groundwater tracing studies. There is often some fluorescence background in or near the range of fluorescein dye present at some of the stations used in groundwater tracing studies.

Criteria for Determining Dye Recoveries

The following sections identify normal criteria used by the OUL for determining dye recoveries. The primary instrument in use is a Shimadzu RF-5301.

EOSINE

Normal Criteria Used by the OUL for Determining Eosine Dye Recoveries in Elutants from Charcoal Samplers

Criterion 1. There must be at least one fluorescence peak in the range of 540.0 to 545.8 nm in the sample.

Criterion 2. The dye concentration associated with the fluorescence peak must be at least 3 times the detection limit. The eosine detection limit in elutant samples is 0.050 ppb, thus this dye concentration limit equals 0.150 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of eosine. Much background fluorescence yields low, broad, and asymmetrical fluorescence peaks rather than the more narrow and symmetrical fluorescence peaks typical of eosine. In addition, there must be no other factors which suggest that the fluorescence peak may not be eosine dye from our groundwater tracing work.

Normal Criteria Used by the OUL for Determining Eosine Dye Recoveries in Water Samples

Criterion 1. In most cases, the associated charcoal samplers for the station should also contain eosine dye in accordance with the criteria listed above. This criterion may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be eosine dye from our groundwater tracing work. The fluorescence peak should generally be in the range of 532.8 to 537.3 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our eosine detection limit in water samples is 0.015 ppb, thus this dye concentration limit equals 0.045 ppb.

Criterion 4. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

FLUORESCEIN

Normal Criteria Used by the OUL for Determining Fluorescein Dye Recoveries in Elutants from Charcoal Samplers

Criterion 1. There must be at least one fluorescence peak in the range of 514.5 to 519.6 nm in the sample.

Criterion 2. The dye concentration associated with the fluorescence peak must be at least 3 times the detection limit. The fluorescein detection limit in elutant samples is 0.025 ppb, thus this dye concentration limit equals 0.075 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of fluorescein. Much background fluorescence yields low, broad, and asymmetrical fluorescence peaks rather than the more narrow and symmetrical fluorescence peaks typical of fluorescein. In addition, there must be no other factors which suggest that the fluorescence peak may not be fluorescein dye from our groundwater tracing work.

Normal Criteria Used by the OUL for Determining Fluorescein Dye Recoveries in Water Samples

Criterion 1. In most cases, the associated charcoal samplers for the station should also contain fluorescein dye in accordance with the criteria listed above. This criterion may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be fluorescein dye from our groundwater tracing work. The fluorescence peak should generally be in the range of 506.8 to 510.6 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our fluorescein detection limit in water samples is 0.002 ppb, thus this dye concentration limit equals 0.006 ppb.

Criterion 4. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

RHODAMINE WT

Normal Criteria Used by the OUL for Determining Rhodamine WT Dye Recoveries in Elutants from Charcoal Samplers

Criterion 1. There must be at least one fluorescence peak in the sample in the range of 565.2 to 571.8 nm.

Criterion 2. The dye concentration associated with the rhodamine WT peak must be at least 3 times the detection limit. The detection limit in elutant samples is 0.170 ppb, thus this dye concentration limit equals 0.510 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of rhodamine WT. In addition, there must be no other factors which suggest that the fluorescence peak may not be dye from the groundwater tracing work under investigation.

Normal Criteria Used by the OUL for Determining Rhodamine WT Dye Recoveries in Water Samples

Criterion 1. In most cases, the associated charcoal samplers for the station should also contain rhodamine WT dye in accordance with the criteria listed above. These criteria may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be rhodamine WT dye from the tracing work under investigation. The fluorescence peak should generally be in the range of 572.4 to 577.7 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our rhodamine WT detection limit in water samples is 0.015 ppb, thus this dye concentration limit is 0.045 ppb.

Criterion 4. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

SULFORHODAMINE B

Normal Criteria Used by the OUL for Determining Sulforhodamine B Dye Recoveries in Elutants from Charcoal Samplers

Criterion 1. There must be at least one fluorescence peak in the sample in the range of 576.4 to 583.2 nm.

Criterion 2. The dye concentration associated with the sulforhodamine B peak must be at least 3 times the detection limit. The detection limit in elutant samples is 0.080 ppb, thus this dye concentration limit equals 0.240 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of sulforhodamine B. In addition, there must be no other factors which suggest that the fluorescence peak may not be dye from the groundwater tracing work under investigation.

Normal Criteria Used by the OUL for Determining Sulforhodamine B dye Recoveries in Water Samples

Criterion 1. In most cases, the associated charcoal samplers for the station should also contain sulforhodamine B dye in accordance with the criteria listed earlier. This criterion may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be sulforhodamine B dye from the tracing work under investigation. The fluorescence peak should generally be in the range of 580.8 to 584.4 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. The detection limit in water is 0.008 ppb, thus this dye concentration limit equals 0.024 ppb.

Criterion 4. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Standard Footnotes

Sometimes not all the criteria are met for a straight forward determination of tracer dye in a sample. For these reasons, the emission graph is scrutinized carefully by the analytical technician and again during the QA/QC process. Sometimes the emission graphs require interpretation as to whether or not a fluorescence peak represents the tracer dye or not. Background samples from each of the sampling stations aid in the interpretation of the emission fluorescence graphs. When the results do not meet all the criteria for a positive dye detection, often the fluorescence peak is quantified and flagged with a footnote to the result as not meeting all the criteria for a positive dye detection. Standard footnotes are as follows:

Single asterisk (*): A fluorescence peak is present that does not meet all the criteria for a positive dye recovery. However, it has been calculated as though it were the tracer dye.

Double asterisk (**): A fluorescence peak is present that does not meet all the criteria for this dye. However, it has been calculated as a positive dye recovery.

Other footnotes specific to the fluorescence signature are sometimes also used. These footnotes are often developed for a specific project.

The quantification of fluorescence peaks that do not meet all the criteria for a positive dye detection can be important for interpretation of the dataset as a whole.

ATTACHMENT 1
Sample Collection Data Sheet

OZARK UNDERGROUND LABORATORY, INC.

1572 Aley Lane Protem, MO 65733 (417) 785-4289 fax (417) 785-4290 email: contact@ozarkundergroundlab.com

SAMPLE COLLECTION DATA SHEET for FLUORESCENCE ANALYSIS

Project _____ **Week No:** ___ **Samples Collected By:** _____

Samples Shipped By: _____ **Samples Received By:** _____

Date Samples Shipped: ___ **Date Samples Received:** ___ **Time Samples Received:** ___ **Return Cooler? Yes** ☐ **No** ☐

Bill to: ___ **Send Results to:** ___

Analyze for: ☐ **Fluorescein** ☐ **Eosine** ☐ **Rhodamine WT** ☐ **Other** _____ **Ship cooler to:** ___

OUL use only		***Please indicate stations where dye was visible in the field*** *for field technician use - use black ink only*						*OUL use only*
# CHAR REC'D	**LAB NUMBER**	**STATION NUMBER 1-4 Numbers**	**STATION NAME**	**PLACED**		**COLLECTED**		**# WATER REC'D**
				DATE	**TIME**	**DATE**	**TIME**	

COMMENTS _____

_____

This sheet filled out by OUL staff? Yes ☐ **No** ☐ **Charts for samples on this page proofed by OUL:** _____

OUL Project No._____ **Date Analyzed:**_____ **Analyzed By:**_____

APPENDIX B

Groundwater Tracing Analytical Results

Table 1.	Results for charcoal samplers analyzed for the presence of fluorescein and rhodamine WT (RWT) dyes.							
	Peak wavelengths are reported in nanometers (nm); dye concentrations are reported in parts per billion (ppb).							
OUL	**Station**	**Station Name**	**Date/Time**	**Date/Time**	**Fluorescein Results**		**RWT Results**	
#	**#**		**Placed**	**Recovered**	**Peak nm**	**Conc. ppb**	**Peak nm**	**Conc. ppb**
Y2225	**1**	**New Cricket Spring**	**11/7/14 1110**	**11/17/14 1040**	**516.2 ***	**3.57**	**ND**	
Y2225D	1	New Cricket Spring	11/7/14 1110	11/17/14 1040	515.8 *	3.79	ND	
Y2229	1	New Cricket Spring	11/17/14 1040	11/18/14 1625	516.3	43,200	567.4	106,000
Y2229D	1	New Cricket Spring	11/17/14 1040	11/18/14 1625	516.2	42,700	567.4	115,000
Y2304	1	New Cricket Spring	11/18/14 1625	11/24/14 1215	516.0	57,600	567.2	210,000
Y2304D	1	New Cricket Spring	11/18/14 1625	11/24/14 1215	516.3	65,000	566.7	197,000
Y2768	1	New Cricket Spring	11/24/14 1215	12/2/14 1110	516.3	11,000	567.3	32,500
Y2768D	1	New Cricket Spring	11/24/14 1215	12/2/14 1110	516.6	12,100	567.2	35,500
Y2775	1	New Cricket Spring	12/2/14 1110	12/8/14 1115	516.2	3,520	567.4	10,200
Y2775D	1	New Cricket Spring	12/2/14 1110	12/8/14 1115	516.2	2,920	567.5	8,780
Y3101	1	New Cricket Spring	12/8/14 1115	12/15/14 1145	516.0	3,180	567.3	10,000
Y3101D	1	New Cricket Spring	12/8/14 1115	12/15/14 1145	516.2	2,250	567.7	7,810
Y3150	1	New Cricket Spring	12/15/14 1145	12/22/14 1010	516.2	647	567.8	3,920
Y3150D	1	New Cricket Spring	12/15/14 1145	12/22/14 1010	516.2	628	567.8	3,480
Y3374	1	New Cricket Spring	12/22/14 1010	12/29/14 1230	516.2	374	569.2	2,820
Y3374D	1	New Cricket Spring	12/22/14 1010	12/29/14 1230	516.2	636	567.6	3,920
Y3395	1	New Cricket Spring	12/29/14 1230	1/5/15 1230	516.1	503	567.5	3,100
Y3395D	1	New Cricket Spring	12/29/14 1230	1/5/15 1230	516.1	586	567.7	3,440
Y3852	1	New Cricket Spring	1/5/15 1230	1/23/15 1340	515.3	194	569.3	2,070
Y3852D	1	New Cricket Spring	1/5/15 1230	1/23/15 1340	516.0	221	568.4	2,630
Y2230	**2**	**Cricket Spring**	**11/17/14 1430**	**11/18/14 1545**	**ND**		**ND**	
Y2305	2	Cricket Spring	11/18/14 1545	11/24/14 1245	ND		ND	
Y2769	2	Cricket Spring	11/24/14 1245	12/2/14 1125	ND		ND	
Y2776	2	Cricket Spring	12/2/14 1125	12/8/14 1300	ND		ND	
Y3102	2	Cricket Spring	12/8/14 1300	12/15/14 1220	ND		ND	
Y3151	2	Cricket Spring	12/15/14 1220	12/22/14 0850	ND		ND	
Y3375	2	Cricket Spring	12/22/14 0850	12/29/14 1315	ND		ND	
Y3396	2	Cricket Spring	12/29/14 1315	1/5/15 1240	ND		ND	
Y3853	2	Cricket Spring	1/5/15 1240	1/23/15 1400	ND		ND	
Y2226	**3**	**RR Tunnel SE; total drainage, east side**	**11/7/14 1500**	**11/17/14 0830**	**ND**		**ND**	
Y3376	3	RR Tunnel SE total drainage east side	11/17/14 0830	12/29/14 1415	ND		ND	
Y2227	**4**	**RR Tunnel SE; total drainage, west side**	**11/7/14 1510**	**11/17/14 0835**	**ND**		**ND**	

Charcoal results
for
Arkwood

OUL	Station	Station Name	Date/Time	Date/Time	Fluorescein Results		RWT Results	
#	#		Placed	Recovered	Peak nm	Conc. ppb	Peak nm	Conc. ppb
Y3377	4	RR Tunnel SE total drainage west side	11/17/14 0835	12/29/14 1400	ND		ND	
Y2306	**5**	**Well A**	**11/18/14 1700**	**11/24/14 1122**	**515.9**	**271**	**ND**	
Y2770	5	Well A	11/24/14 1122	12/2/14 1230	516.6	3.65	569.0	5.84
Y2777	5	Well A	12/2/14 1230	12/8/14 1250	515.5	9.63	ND	
Y3152	5	Well A	12/8/14 1250	12/22/14 0915	515.7	18.9	569.6	0.839
Y3397	5	Well A	12/22/14 0915	1/5/15 1050	515.8	22.3	570.0	57.5
Y2307	**6**	**Well B**	**11/18/14 1715**	**11/24/14 1130**	**ND**		**569.5**	**526**
Y3398	6	Well B	11/24/14 1130	1/5/15 1055	ND		569.4	640
Y2308	**7**	**Well C**	**11/17/14 1015**	**11/24/14 1050**	**ND**		**ND**	
Y3399	7	Well C	11/24/14 1050	1/5/15 1100	ND		571.0	0.786
Y2309	**8**	**Well D**	**11/17/14 0930**	**11/24/14 1028**	**ND**		**ND**	
Y3401	8	Well D	11/24/14 1028	1/5/15 1105	ND		ND	
Y2310	**9**	**Well E**	**11/17/14 0940**	**11/24/14 1110**	**516.0**	**32,900**	**567.6**	**163**
Y2771	9	Well E	11/24/14 1110	12/2/14 1240	516.3	3,630	ND	
Y2778	9	Well E	12/2/14 1240	12/8/14 1220	515.1	15.5	ND	
Y3153	9	Well E	12/8/14 1220	12/22/14 0925	515.8	3.86	569.8	12.6
Y3402	9	Well E	12/22/14 0925	1/5/15 1110	515.8	3.14	569.6	4.49
Y2311	**10**	**Well F**	**11/17/14 0945**	**11/24/14 1105**	**516.2**	**6,200**	**567.0**	**105**
Y2772	10	Well F	11/24/14 1105	12/2/14 1250	514.9	6.34	ND	
Y2779	10	Well F	12/2/14 1250	12/8/14 1230	515.2	1.90	ND	
Y3154	10	Well F	12/8/14 1230	12/22/14 0930	515.3	1.35	ND	
Y3403	10	Well F	12/22/14 0930	1/5/15 1115	514.8	0.753	569.6	13.4
Y2312	**11**	**Well G**	**11/17/14 0950**	**11/24/14 1033**	**515.5**	**1.96**	**568.3**	**72.4**
Y3404	11	Well G	11/24/14 1033	1/5/15 1120	ND		569.6	3.93
Y2313	**12**	**Well H**	**11/17/14 0955**	**11/24/14 1005**	**ND**		**ND**	
Y3405	12	Well H	11/24/14 1005	1/5/15 1125	ND		ND	
Y2314	**13**	**Well I**	**11/17/14 1000**	**11/24/14 1038**	**ND**		**ND**	
Y3406	13	Well I	11/24/14 1038	1/5/15 1130	ND		ND	
Y2315	**14**	**Well J**	**11/17/14 1010**	**11/24/14 1045**	**ND**		**ND**	
Y2773	14	Well J	11/24/14 1045	12/2/14 1300	515.6 *	0.395	ND	
Y2781	14	Well J	12/2/14 1300	12/8/14 1240	515.0 *	0.406	ND	
Y3155	14	Well J	12/8/14 1240	12/22/14 0940	515.0 *	0.890	ND	
Y3407	14	Well J	12/22/14 0940	1/5/15 1135	516.2 *	0.769	569.4	6.70
Y2316	**15**	**Well K**	**11/17/14 1005**	**11/24/14 1055**	**ND**		**ND**	

Charcoal results
for
Arkwood

OUL #	Station #	Station Name	Date/Time Placed	Date/Time Recovered	Fluorescein Results		RWT Results	
					Peak nm	Conc. ppb	Peak nm	Conc. ppb
Y3156	15	Well K	11/24/14 1055	12/22/14 0945	ND		ND	
Y3408	15	Well K	12/22/14 0945	1/5/15 1140	516.6	0.538	568.0	2.09
Y2228	**16**	**Cricket Pond Discharge**	**11/7/14 1255**	**11/17/14 1050**	**517.2 ***	**0.566**	**565.6 ***	**3.59**
Y2231	16	Cricket Pond Discharge	11/17/14 1050	11/18/14 1550	ND		ND	
Y2317	16	Cricket Pond Discharge	11/18/14 1550	11/24/14 1230	515.3	9.13	567.7	34.2
Y2774	16	Cricket Pond Discharge	11/24/14 1230	12/2/14 1130	516.0	0.722	568.2	11.3
Y2782	16	Cricket Pond Discharge	12/2/14 1130	12/8/14 1310	515.3	27.8	568.8	159
Y3103	16	Cricket Pond Discharge	12/8/14 1310	12/15/14 1230	515.5	7.20	568.1	99.9
Y3157	16	Cricket Pond Discharge	12/15/14 1230	12/22/14 0900	515.5	4.44	568.1	48.2
Y3378	16	Cricket Pond Discharge	12/22/14 0900	12/29/14 1325	515.4	3.31	568.0	30.8
Y3409	16	Cricket Pond Discharge	12/29/14 1325	1/5/15 1250	515.6	7.70	568.3	46.7
Y3854	16	Cricket Pond Discharge	1/5/15 1250	1/23/15 1410	515.4	2.50	568.6	43.5

APPENDIX C

Calculations for RPD and Mass Balance

Table C-2. Composite water samples - RPD Calculations

Peak wavelengths are reported in nanometers (nm); dye concentrations are reported in parts per billion (ppb).

OUL	Station	Station Name	Started	Ended	Fluorescein Results				RWT Results			
Number	Number		Date/Time	Date/Time	Peak nm	Conc. ppb	Mean (ppb)	RPD	Peak nm	Conc. ppb	Mean (ppb)	RPD
Y2233	100	New Cricket Spring-Comp	11/8/14 0500	11/8/14 1200	506.2 *	0.043			--	ND		
Y2233R	100	New Cricket Spring-Comp	11/8/14 0500	11/8/14 1200	506.2 *	0.042	0.043	2.4%	--	ND	ND	--
Y2235	100	New Cricket Spring-Comp	11/10/14 0500	11/10/14 1200	506.4 *	0.041			--	ND		
Y2235R	100	New Cricket Spring-Comp	11/10/14 0500	11/10/14 1200	505.4 *	0.040	0.041	2.5%	--	ND	ND	--
Y2239	100	New Cricket Spring-Comp	11/14/14 0500	11/14/14 1200	505.6 *	0.030			--	ND		
Y2239R	100	New Cricket Spring-Comp	11/14/14 0500	11/14/14 1200	505.6 *	0.028	0.029	6.9%	--	ND	ND	--
Y2322	100	New Cricket Spring-Comp	11/19/14 0500	11/19/14 1200	507.5	1,350			574.2	4,680		
Y2322R	100	New Cricket Spring-Comp	11/19/14 0500	11/19/14 1200	507.6	1,310	1330	3.0%	574.1	4,240	4,460	9.9%
Y2325	100	New Cricket Spring-Comp	11/20/14 0500	11/20/14 1200	507.6	1,900			574.1	5,020		
Y2325R	100	New Cricket Spring-Comp	11/20/14 0500	11/20/14 1200	508.0	1,870	1890	1.6%	574.3	4,560	4,790	9.6%
Y2328	100	New Cricket Spring-Comp	11/21/14 0500	11/21/14 1200	507.4	755			574.1	2,220		
Y2328R	100	New Cricket Spring-Comp	11/21/14 0500	11/21/14 1200	507.4	780	768	3.3%	574.1	2,300	2,260	3.5%
Y2331	100	New Cricket Spring-Comp	11/22/14 0500	11/22/14 1200	507.3	450			574.1	1,420		
Y2331R	100	New Cricket Spring-Comp	11/22/14 0500	11/22/14 1200	507.3	445	448	1.1%	574.2	1,410	1,415	0.7%
Y2334	100	New Cricket Spring-Comp	11/23/14 0500	11/23/14 1200	507.5	271			574.5	942		
Y2334R	100	New Cricket Spring-Comp	11/23/14 0500	11/23/14 1200	507.5	275	273	1.5%	574.4	939	941	0.3%
Y2337	100	New Cricket Spring-Comp	11/24/14 0500	11/24/14 1200	507.4	180			574.3	673		
Y2337R	100	New Cricket Spring-Comp	11/24/14 0500	11/24/14 1200	507.4	185	183	2.7%	574.3	643	658	4.6%
Y2785	100	New Cricket Spring-Comp	11/24/14 0500	11/25/14 1200	507.4	156			574.2	512		
Y2785R	100	New Cricket Spring-Comp	11/25/14 0500	11/25/14 1200	507.4	154	155	1.3%	574.1	521	517	1.7%
Y2788	100	New Cricket Spring-Comp	11/26/14 0500	11/26/14 1200	507.3	228			573.8	632		
Y2788R	100	New Cricket Spring-Comp	11/26/14 0500	11/26/14 1200	507.2	219	224	4.0%	574.2	614	623	2.9%
Y2791	100	New Cricket Spring-Comp	11/27/14 0500	11/27/14 1200	507.3	133			574.6	407		
Y2791R	100	New Cricket Spring-Comp	11/27/14 0500	11/27/14 1200	507.2	137	135	3.0%	574.2	428	418	5.0%
Y2794	100	New Cricket Spring-Comp	11/28/14 0500	11/28/14 1200	507.3	90.4			574.2	302		
Y2794R	100	New Cricket Spring-Comp	11/28/14 0500	11/28/14 1200	507.3	90.6	90.5	0.2%	574.3	298	300	1.3%
Y2797	100	New Cricket Spring-Comp	11/29/14 0500	11/29/14 1200	507.3	70.2			574.2	244		
Y2797R	100	New Cricket Spring-Comp	11/29/14 0500	11/29/14 1200	507.3	68.2	69.2	2.9%	574.3	235	240	3.8%
Y2801	100	New Cricket Spring-Comp	11/30/14 0500	11/30/14 1200	507.3	59.5			574.3	209		
Y2801R	100	New Cricket Spring-Comp	11/30/14 0500	11/30/14 1200	507.3	60.0	59.8	0.8%	574.3	201	205	3.9%
Y2804	100	New Cricket Spring-Comp	12/1/14 0500	12/1/14 1200	507.4	50.9			574.3	189		
Y2804R	100	New Cricket Spring-Comp	12/1/14 0500	12/1/14 1200	507.4	51.6	51.3	1.4%	574.3	185	187	2.1%
Y2807	100	New Cricket Spring-Comp	12/2/14 0500	12/2/14 1200	507.5	47.5			574.3	183		

OUL	Station	Station Name	Started	Ended	Fluorescein Results				RWT Results			
Number	Number		Date/Time	Date/Time	Peak nm	Conc. ppb	Mean (ppb)	RPD	Peak nm	Conc. ppb	Mean (ppb)	RPD
Y2807R	100	New Cricket Spring-Comp	12/2/14 0500	12/2/14 1200	507.5	46.8	47.2	1.5%	574.3	176	180	3.9%
Y2809	100	New Cricket Spring-Comp	12/3/14 0100	12/3/14 1200	507.4	41.6			574.3	157		
Y2809R	100	New Cricket Spring-Comp	12/3/14 0100	12/3/14 1200	507.5	40.4	41.0	2.9%	574.3	151	154	3.9%
Y2811	100	New Cricket Spring-Comp	12/4/14 0100	12/4/14 1200	507.4	37.1			574.3	144		
Y2811R	100	New Cricket Spring-Comp	12/4/14 0100	12/4/14 1200	507.5	36.3	36.7	2.2%	574.3	140	142	2.8%
Y2813	100	New Cricket Spring-Comp	12/5/14 0100	12/5/14 1200	507.3	34.8			574.3	139		
Y2813R	100	New Cricket Spring-Comp	12/5/14 0100	12/5/14 1200	507.5	33.3	34.1	4.4%	574.3	135	137	2.9%
Y2815	100	New Cricket Spring-Comp	12/6/14 0100	12/6/14 1200	507.3	12.8			574.3	52.8		
Y2815R	100	New Cricket Spring-Comp	12/6/14 0100	12/6/14 1200	507.5	12.6	12.7	1.6%	574.3	50.6	52	4.3%
Y2817	100	New Cricket Spring-Comp	12/7/14 0100	12/7/14 1200	507.4	10.3			574.3	47.6		
Y2817R	100	New Cricket Spring-Comp	12/7/14 0100	12/7/14 1200	507.4	10.5	10.4	1.9%	574.2	47.9	48	0.6%
Y2819	100	New Cricket Spring-Comp	12/8/14 0100	12/8/14 1200	507.3	16.9			574.3	60.1		
Y2819R	100	New Cricket Spring-Comp	12/8/14 0100	12/8/14 1200	507.5	16.6	16.8	1.8%	574.2	58.6	59	2.5%
Y3105	100	New Cricket Spring-Comp	12/9/14 0100	12/9/14 1200	507.2	26.7			574.1	79.9		
Y3105R	100	New Cricket Spring-Comp	12/9/14 0100	12/9/14 1200	507.3	27.3	27.0	2.2%	574.3	79.8	80	0.1%
Y3110	100	New Cricket Spring-Comp	12/11/14 1300	12/11/14 2359	507.5	11.3			574.3	53.6		
Y3110R	100	New Cricket Spring-Comp	12/11/14 1300	12/11/14 2359	507.5	11.3	11.3	0.0%	574.3	53.8	54	0.4%
Y3115	100	New Cricket Spring-Comp	12/14/14 0100	12/14/14 1200	507.5	9.79			574.3	49.5		
Y3115R	100	New Cricket Spring-Comp	12/14/14 0100	12/14/14 1200	507.6	9.87	9.83	0.8%	574.3	49.1	49	0.8%
Y3161	100	New Cricket Spring-Comp	12/16/14 1300	12/16/14 2359	507.1	4.53			574.2	25.8		
Y3161R	100	New Cricket Spring-Comp	12/16/14 1300	12/16/14 2359	507.2	4.48	4.51	1.1%	574.3	25.6	26	0.8%
Y3165	100	New Cricket Spring-Comp	12/18/14 1300	12/18/14 2359	507.1	2.71			574.3	15.3		
Y3165R	100	New Cricket Spring-Comp	12/18/14 1300	12/18/14 2359	507.2	2.67	2.69	1.5%	574.3	14.9	15	2.6%
Y3170	100	New Cricket Spring-Comp	12/21/14 0100	12/21/14 1200	507.2	4.04			574.1	25.4		
Y3170R	100	New Cricket Spring-Comp	12/21/14 0100	12/21/14 1200	507.3	4.05	4.05	0.2%	574.2	25.5	25	0.4%
Y3384	100	New Cricket Spring-Comp	12/24/14 0100	12/24/14 1200	507.3	4.28			574.1	26.7		
Y3384R	100	New Cricket Spring-Comp	12/24/14 0100	12/24/14 1200	507.4	4.28	4.28	0.0%	574.2	26.4	27	1.1%
Y3389	100	New Cricket Spring-Comp	12/26/14 1300	12/26/14 2359	507.5	4.23			574.3	26.7		
Y3389R	100	New Cricket Spring-Comp	12/26/14 1300	12/26/14 2359	507.4	4.22	4.23	0.2%	574.2	26.1	26	2.3%
Y3394	100	New Cricket Spring-Comp	12/29/14 0100	12/29/14 1200	507.3	4.00			574.3	26.9		
Y3394R	100	New Cricket Spring-Comp	12/29/14 0100	12/29/14 1200	507.4	4.00	4.00	0.0%	574.4	26.1	27	3.0%
Y3414	100	New Cricket Spring-Comp	12/31/14 1300	12/31/14 2359	507.3	4.00			574.2	25.2		
Y3414R	100	New Cricket Spring-Comp	12/31/14 1300	12/31/14 2359	507.4	3.99	4.00	0.3%	574.3	24.4	25	3.2%
Y3419	100	New Cricket Spring-Comp	1/3/15 0100	1/3/15 1200	507.3	3.04			574.3	18.2		
Y3419R	100	New Cricket Spring-Comp	1/3/15 0100	1/3/15 1200	507.3	3.13	3.09	2.9%	574.2	18.3	18	0.5%

APPENDIX D

Study Work Plan

REVISED FINAL
SUPPLEMENTAL GROUNDWATER TRACING STUDY WORK PLAN
ARKWOOD SUPERFUND SITE, OMAHA, ARKANSAS

October 7, 2014

Thomas Aley, PHG & PG
President
Ozark Underground Laboratory, Inc.

A work plan prepared for Ms. Jean Mescher, McKesson Corporation, One Post Street, 34th Floor, San Francisco, CA 94104

Introduction

The Arkwood site is located on relatively flat-lying Boone Formation of Mississippian age. The Boone Formation is comprised primarily of limestone and chert and the abundance of chert varies both laterally and vertically within the formation.

The epikarst is the weathered zone in the upper part of the bedrock. This zone in the Boone Formation is often about 30 feet thick with the abundance of solutional voids decreasing with depth. Residual wastes at waste sites in karst landscapes are commonly detained within the epikarst (also called the epikarstic zone).

In 1991 the Ozark Underground Laboratory (OUL) conducted a comprehensive groundwater tracing study at the Arkwood site with extensive off-site sampling. Dyes for that study were introduced at locations that bracketed the site. One trace was introduced south of the former Woodchip Pile (see Figure 1) and the second was introduced into the flow from New Cricket Spring. A total of 79 sampling stations were monitored during the 1991 dye tracing study. Dye from the Woodchip Pile trace was detected at 12 stations in the Walnut Creek basin and dye from the New Cricket Spring trace was detected at 14 stations within or near the channels of New Cricket Spring Branch and Cricket Creek.

When the facility was in operation, PCP contaminated wastes were dumped into a sinkhole located roughly in the middle of the site. As much debris as possible was subsequently removed from the sinkhole and it was capped with concrete. Several shallow wells into the epikarstic zone were later drilled surrounding the sinkhole area and ozonated water was introduced into some of them to accelerate waste treatment being provided for water discharging from New Cricket Spring.

Nine wells were drilled in the vicinity of the former sinkhole (see Figure 2). The purpose of these wells was to inject ozonated water to enhance treatment of wastes detained in the epikarst. The injected water was also designed to ensure that New Cricket Spring would always have a sufficient flow rate to allow the treatment plant to operate properly. The rate at which individual wells could accept water varied from less than about 1 gallon per minute to 35 gallons per minute or more. Rates of water acceptance decreased with time at some of the wells.

Additional information on the nine wells is as follows: Wells A, B, and C are approximately 25 feet deep. The lower 10 feet of the casing is slotted. Bentonite grout seal is located from a depth of about 10 feet to 2 feet below ground surface. Well D is a casing placed in the location of a former tree. The two holes without letter designations were not completed and were abandoned. Figure 3 provides information on the wells completed in 2007.

Figure 1. Location of dye introduction point 91-01.

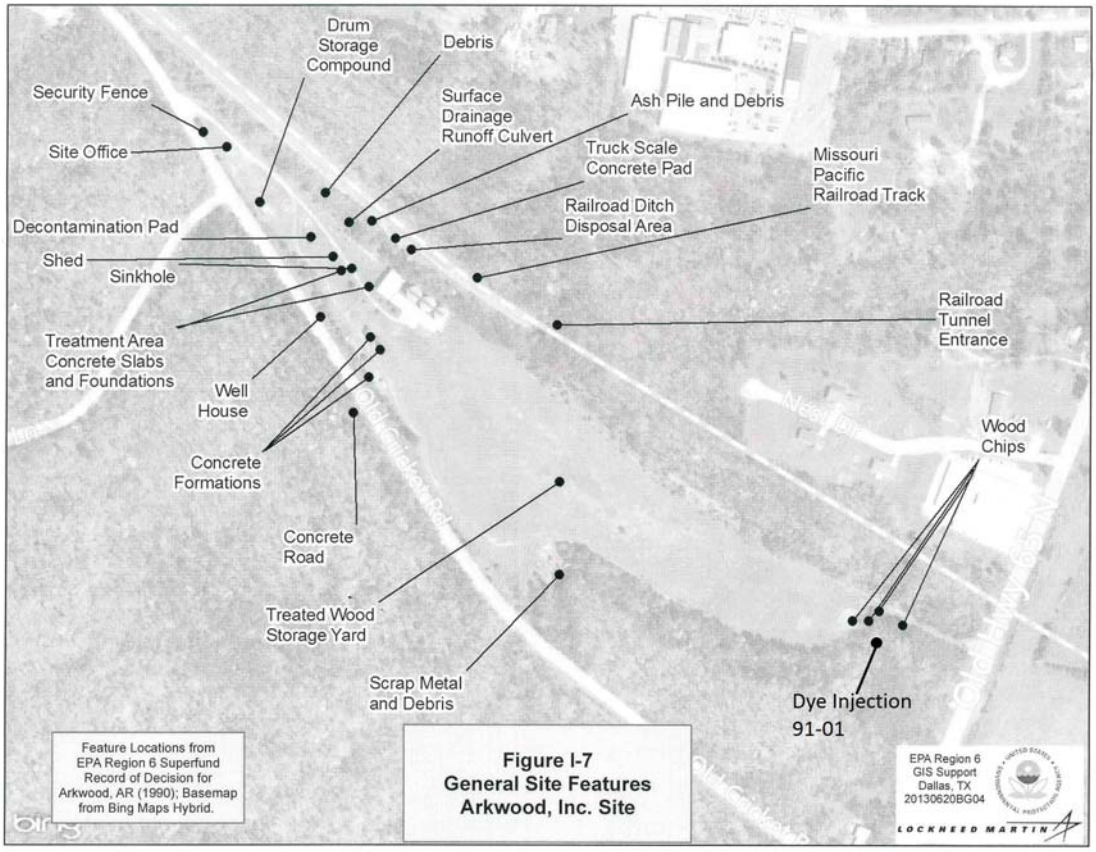


Figure 2. Sketch map showing the relative location of nine wells in the vicinity of the former sinkhole.

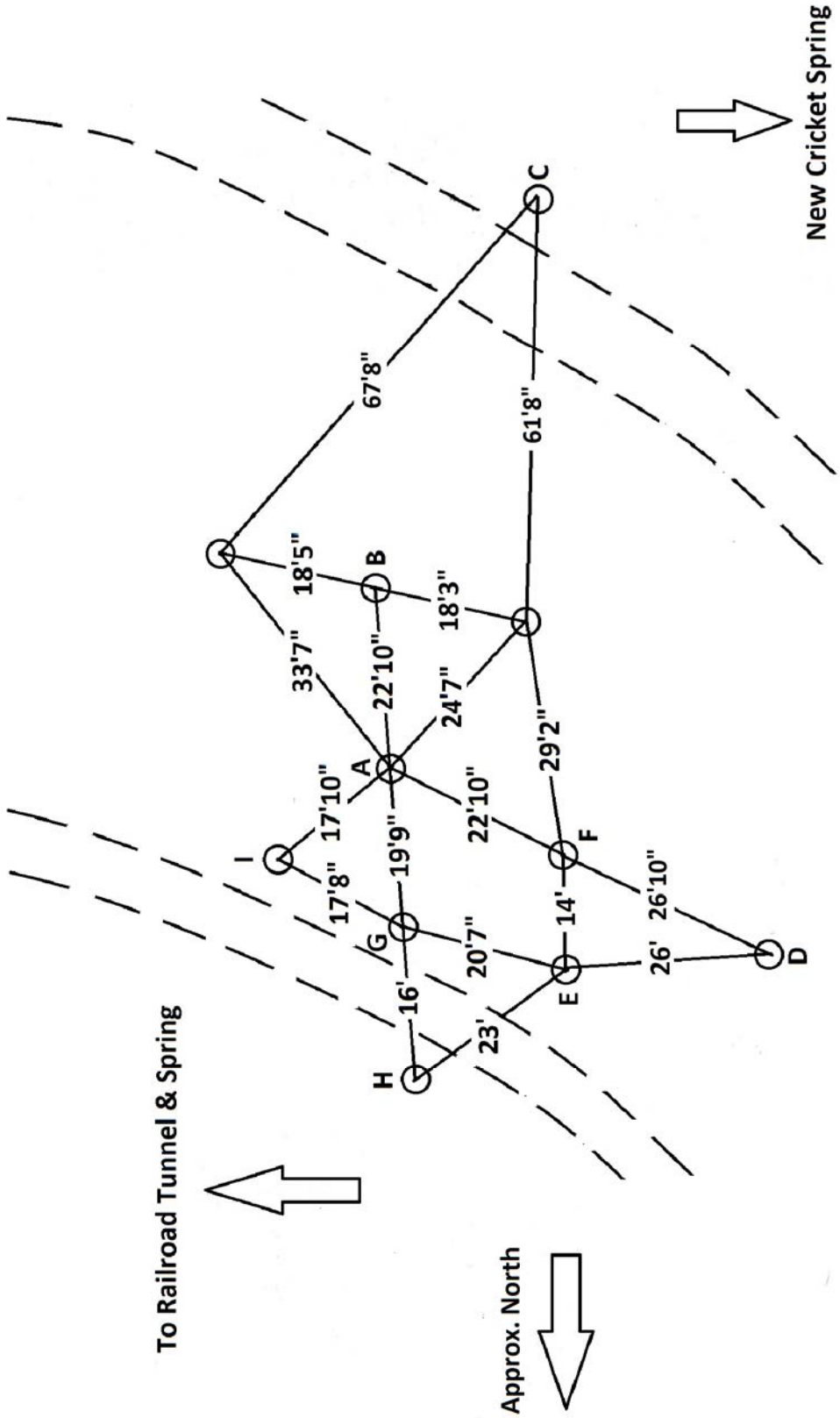
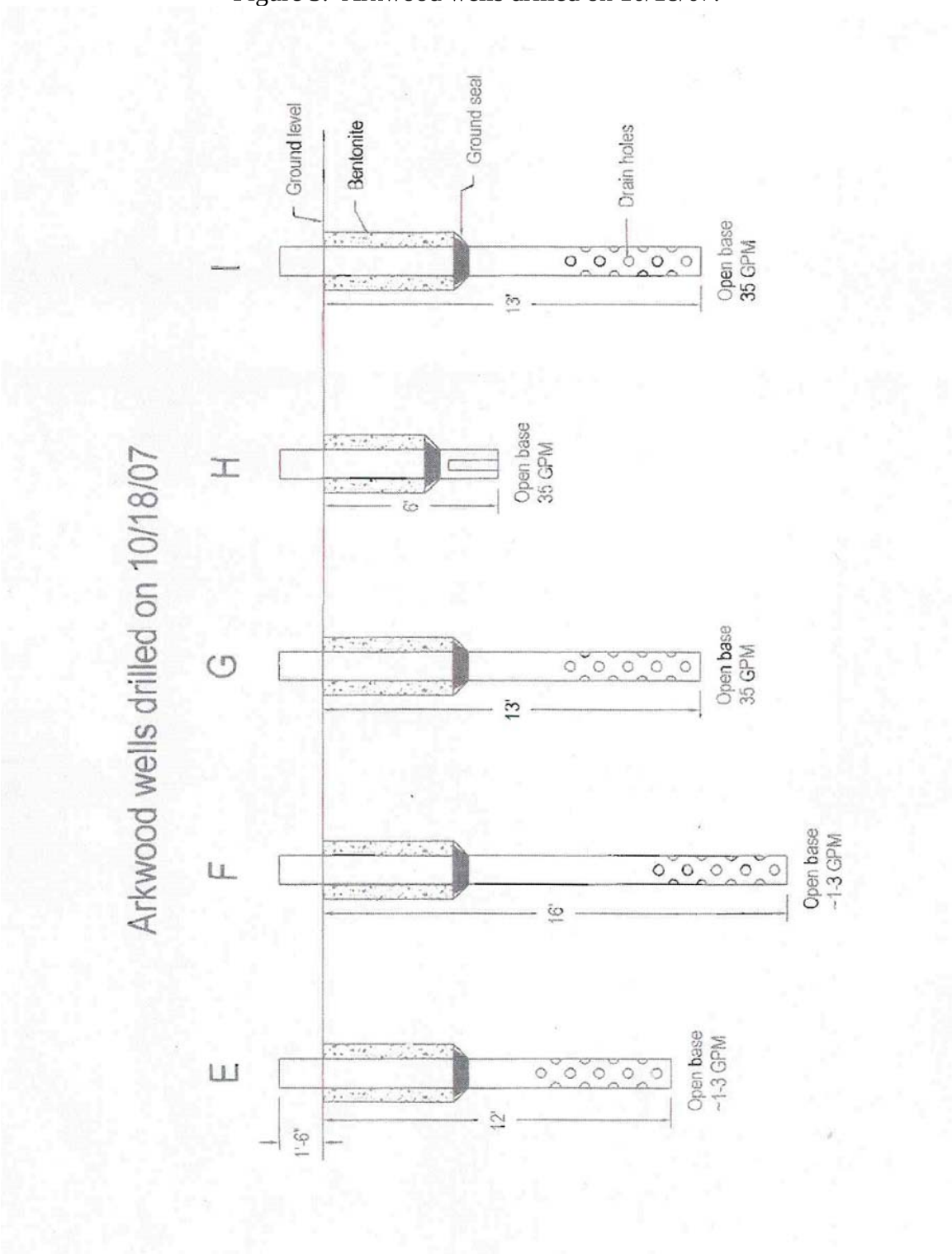


Figure 3. Arkwood wells drilled on 10/18/07.



In March 2014, McKesson Corporation hosted a tour of the site and facilitated on-site discussions for involved personnel from U.S. EPA and Arkansas Department of Environmental Quality (ADEQ). One topic raised during the tour and discussions was the potential benefit of conducting a quantitative dye trace from the vicinity of the former sinkhole to New Cricket Spring. Such a trace would provide data about water movement from that portion of the site most heavily impacted by PCP wastes and associated dioxins to the primary point where contaminated groundwater discharged to the surface. This work plan outlines how such a tracer study would be conducted.

Study Design

Attachment 1 is a copy of the Ozark Underground Laboratory's "Procedures and Criteria Document for Analysis of Fluorescent Dyes in Water and Charcoal Samplers." These procedures and criteria will be followed in the planned dye tracing study.

Two tracer dyes will be utilized at the same time to conduct the tracing study. Fluorescein and rhodamine WT dyes are ideal for use at the site since their emission fluorescence peaks are substantially different and thus do not interfere appreciably with one another unless concentrations of one dye produce a fluorescence peak more than about two orders of magnitude greater than the other. This is not expected at the site.

Prior to any dye or water introduction we will determine if there is any standing water in the selected wells. If there is, we will measure the depth to water below ground surface.

The wells planned for dye introduction are wells A and B. Both wells are located in the vicinity of the former sinkhole. Wells A and B are approximately 25 feet deep. The lower 10 feet of the casing is slotted. Bentonite grout seal is located from a depth of about 10 feet to 2 feet below ground surface.

Prior to any dye introduction we will test wells A and B with about 200 gallons of water in each to verify that they will readily accept water. We anticipate that these wells will readily accept water, but will select an alternate well in the unlikely event that this is necessary. Figure 1 is a sketch of the well locations. New Cricket Spring is northwest of the wells and is about 1,200 feet from the middle of the group of wells. Water for testing the wells and for the dye introductions will be from the deep well on site; it has a reported capacity of about 35 gallons per minute.

One pound of fluorescein dye mixture containing about 75% dye equivalent (a powder mixture) will be mixed with about a gallon of water and introduced into Well A. Four pounds of rhodamine WT dye mixture containing about 20% dye equivalent (a liquid mixture) will be introduced into Well B. Each of the dye introductions will be flushed with approximately equal volumes of water derived from the deep well on site. This well can deliver approximately 35 gallons per minute. A hose or hoses will be run from the deep well to Wells A and B. As much water as possible will be introduced into these wells during a one-day work period. As an estimate, if we can deliver about 35

gallons of water per minute, and can do this for about 5 hours, this would represent a total volume of about 10,000 gallons of water or about 5,000 gallons for each well. A minimum volume of water for each well will be about 2,000 gallons.

New Cricket Spring will be the primary dye sampling station. An ISCO programmable automatic pumped sampler will be installed at the spring (hopefully inside the treatment building). It can collect up to 26 bottles of water before servicing. It will be programmed to collect water samples as follows:

- Three bottles of water per day for the first week after dye introduction. Each bottle will contain a composite water sample consisting of eight equal volumes of water collected at one-hour intervals.
- Two bottles of water per day for the next six weeks. Each bottle will contain a composite water sample consisting of six equal volumes of water collected at two-hour intervals.

We anticipate that most of the dye that discharges from New Cricket Spring will pass through the spring within 7 weeks of the time of dye introduction. In the event that sample analysis after the first 4 weeks of sampling indicates that the duration of a major portion of the dye pulse is likely to last longer than seven weeks, we will recommend that the study be extended for one or more three-week sampling cycles.

Activated carbon samplers will also be placed at New Cricket Spring as control samples. They will be collected and new samplers will be placed each time a trip is made to the site to service the ISCO sampler.

To verify that no dye discharges at locations other than New Cricket Spring, the following locations will be sampled with activated carbon samplers and grab samples of water:

- Cricket Spring (located downstream of New Cricket Spring)
- Water discharging from the south end of the railroad tunnel and, depending upon flow conditions, at one or two additional sites in upstream portions of the Walnut Creek Valley. This assumes that access to the area can be obtained.

Tracer dyes will be introduced in two of the nine wells near the former sinkhole. All nine wells will be sampled for tracer dyes each time the ISCO sampler is serviced. This sampling will use activated carbon samplers (which sample continuously) and grab samples of water. All carbon samplers will be analyzed. Water samples will be analyzed each time one or more of the tracer dyes is detected in the associated carbon sampler. Sampling will use bailers dedicated to each well; activated carbon samplers will be attached to the bailers. Water samples will be analyzed only if one or both of the dyes is detected in the associated activated carbon sampler. These data will help assess water movement among wells in the epikarstic zone.

Continuous flow records will be collected at New Cricket Spring except when the flow rate exceeds 650 gpm. When flow is greater than 650 gpm the excess flow passes

through a 90-degree V-notch weir for which there is a rating table and can be manually recorded up to approximately 1300 gpm. A pressure transducer will be used during the study period to record water depth upstream of the weir. Through a combination of the two types of flow records we will be able to determine the total flow [1]rates from New Cricket Spring during the study period. These flow rates, multiplied by dye concentrations will permit calculation of the cumulative mass of dye discharged through New Cricket Spring.

Some of the mass of dye introduced will remain in close proximity to the well where it was introduced and more will be adsorbed on soil and rock surfaces. The technical literature suggests that dye traces from sinkholes to springs are typically characterized by 20 to 50% of the introduced dye being detected at the spring. The percent of recovery probably will be greater for fluorescein than rhodamine WT because rhodamine WT has a greater sorption tendency.

Given the amount of dye planned for use and the anticipated rapid flow from the introduction points to the spring we anticipate that the percent recovery will be near the upper limit of that typical for traces from sinkholes to springs.

Rather than focusing on the mass of dye recovered, the better approach is to determine the amount of time required for 50% of the detected dye to discharge from the spring and the time required for 90% of it to discharge.

Sampling for tracer dye at Cricket Spring (a site different from New Cricket Spring), in drainage from the Railroad Tunnel, and in Walnut Creek is expected to verify that none of the introduced dyes bypass New Cricket Spring.

Reports

A final report will be prepared at the completion of the study. The report will include all relevant data including dye analysis results.

Submitted:

Tom Aley, President
Ozark Underground Laboratory, Inc.

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